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SMALL-SCALE PELLET BOILER EMISSIONS – CHARACTERIZATION AND COMPARISON TO OTHER COMBUSTION UNITS

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Academic Dissertation

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ABSTRACT

Residential combustion has been identified as one of the main sources of particulate matter (PM); fine particles are important because of their adverse effects on human health and the environment. In this thesis, fine particle emissions originating from residential pellet combustion were characterized in different operational situations and using different raw materials as pellet fuel. Moreover, pellet combustion emissions were compared with those from other combustion technologies used for heat production, including batch-wise operated wood stoves, residential-scale oil boilers and medium-scale plants utilizing wood chips and heavy fuel oil.

Particle emissions from pellet combustion in modern pellet boilers are low compared to those of other wood-fueled residential appliances; these particles primarily consist of fine inorganic fly ash. Decreasing air-to-fuel ratio of primary combustion while increasing air-to-fuel ratio of secondary combustion affected the release of fine fly ash without deteriorating the combustion conditions, resulting in significant reductions in fine particle emissions. In low-load conditions, the amount of fine fly ash particles remained constant, but fine particle emissions increased due to soot formation.

The pellet raw material largely affected fuel originated fine fly ash emissions, whereas emissions of incomplete combustion remained low. The addition of peat to biomass fuels was found to decrease fine particle emissions due to the increased binding of alkali metals in the bottom ash. The use of bark or straw pellets resulted in elevated fine fly ash particle emissions because of the larger alkali metal contents in the fuel. Thus, only stem-wood-based pellets should be used in current residential-scale combustion technology to prevent additional particle emissions.

Combustion technology had a substantial effect on particle and gaseous emissions in the studied batch-wise operated appliances, although the emissions are generally higher than from pellet combustion. In batch combustion, fine particles are mainly formed of elemental carbon and organic matter, although fine fly ash is also present in these particles. Based on the analyzed particle components, polycyclic aromatic hydrocarbons (PAHs) were found to be the most sensitive compound for combustion quality, indicating that the harmfulness of PM from different sources may vary more than what is estimated for particle mass emissions alone.

Although particle emissions from light fuel oil combustion are low, this combustion produces more PAHs than pellet combustion. Heavy fuel oil exhibited similar PM emissions as pellet boilers; however, significantly more PAHs and heavy metals were also produced.

There are numerous options for reducing emissions using combustion technology and flue-gas cleaning. Overall, combustion technology provides the possibility of decreasing emissions from residential combustion; however, firmer emission regulations are needed to increase the utilization of low-emission technologies.

Keywords: aerosol, air pollutions, agricultural fuel, biomass, boiler, emission characterization, fine particle emissions, masonry heater, particulate matter, peat, pellets, residential combustion, small-scale combustion

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Heikki Lamberg

Abbreviations

CMH=conventional masonry heater
CO_3=carbonate carbon
DGI=Dekati Gravimetric Impactor
DLPI=Dekati Low-Pressure Impactor
DR=dilution ratio
EC=elemental carbon (soot)
ED=ejector diluter
ELPI=Electrical Low-Pressure Impactor
ESP=electrostatic precipitator
FMPS=Fast Mobility Particle Sizer Spectrometer
GC-MS=Gas Chromatography Mass Spectrometry
HFO=heavy fuel oil
ICP-AES=Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS=Inductively Coupled Plasma Mass Spectrometry
ISO=International Organization for Standardization
LFO=light fuel oil
MMH=modern masonry heater
NO_X=nitrogen oxides
OC=organic carbon
OGC=organic gaseous compounds
OM=organic matter
PAH=polycyclic aromatic hydrocarbons
PB=pellet boiler
PCDD/F=polychlorinated dibentzodioxins/furans
PM_1 ($PM_{2.5}$, PM_{10})=Mass of particles below aerodynamic diameter of 1 µm (2.5 µm, 10 µm)
POM=particulate organic matter
PRD=porous tube diluter
SOA=secondary organic aerosol
SO_X=sulfur oxides
SS=sauna stove
VOC=volatile organic compounds
λ=air-to-fuel ratio

List of publications

This thesis is based on four publications that are referred to in the text using Roman numerals (i.e., I-IV). The publications are reproduced with the kind permission of the respective journals.

Paper I Lamberg, H., Sippula, O., Tissari, J., Jokiniemi, J. (2011). Effects of Air Staging and Load on Fine-Particle and Gaseous Emissions from a Small-Scale Pellet Boiler. *Energy & Fuels* 25, 4952–4960.

Paper II Lamberg, H., Nuutinen, K., Tissari, J., Ruusunen, J., Yli-Pirilä, P., Sippula, O., Tapanainen, M., Jalava, P., Makkonen, U., Teinilä, K., Saarnio, K., Hillamo, R., Hirvonen, M.-R., Jokiniemi, J. (2011). Physicochemical characterization of fine particles from small-scale wood combustion. *Atmospheric Environment* 45, 7635–7643.

Paper III Lamberg, H., Tissari, J., Jokiniemi, J., Sippula, O. (2013). Fine Particle and Gaseous Emissions from a Small-Scale Boiler Fueled by Pellets of Various Raw Materials. *Energy & Fuels* 27, 7044–7053.

Paper IV Kaivosoja, T., Jalava, P.I., Lamberg, H., Virén, A., Tapanainen, M., Torvela, T., Tapper, U., Sippula, O., Tissari, J., Hillamo, R., Hirvonen, M.-R., Jokiniemi, J. (2013). Comparison of emissions and toxicological properties of fine particles from wood and oil boilers in small (20–25 kW) and medium (5–10 MW) scale. *Atmospheric Environment* 77, 193–201.

Contents

1 INTRODUCTION

Particulate matter (PM) is defined as the total mass of suspended particles in the air. PM is typically divided into three subclasses, i.e., PM_{10}, $PM_{2.5}$ and $PM_{0.1}$, which are defined as particle matter with an aerodynamic diameter smaller than 10 μm, 2.5 μm and 0.1 μm, respectively. $PM_{2.5}$ particles are generally called "fine particles"; however, this term can also be applied to the number or surface area based on particle diameters less than 2.5 μm. In the atmosphere, particles can be solid or liquid; the mixture of particles and gases is called "aerosol".

Fine particles originate from natural and anthropogenic sources. Examples of natural sources include volcanoes, natural forest fires, biogenic aerosols, windborne dust and sea spray (Andreae and Crutzen 1997, Seinfeld and Pandis 1998). The most important sources of anthropogenic particles are different types of combustion processes, such as domestic heating, power plants and internal combustion engines. When particles from combustion sources are discussed, particles with aerodynamic diameters less than 1 μm or 2.5 μm (PM_1 or $PM_{2.5}$) are often used, whereas particles with sizes ranging from 2.5 μm to 10 μm are called coarse particles. Examples of coarse particle sources include road wear and wind-blown dust. On the contrary to primary particles, which are directly emitted from various sources in particulate form, secondary particles are formed in the atmosphere through gas-to-particle conversion processes. The most common types of secondary aerosol formation are sulfur dioxide (SO_2) and nitrogen oxide (NO_X) reactions in the atmosphere and the oxidation of organic gases. The products of the latter mechanism are generally referred to as secondary organic aerosols (SOAs). Primary and secondary particles form the total particulate matter in the atmosphere. These particles constantly interact with their surroundings.

Fine particles are known to have adverse effects on human health and to cause respiratory and cardiac symptoms and even premature death, especially among those with reduced health conditions, e.g., children, elderly and those with chronic diseases (Dockery and Pope 1994, Pope et al. 2002). Recently, the IARC has classified outdoor air pollution and particulate matter from outdoor air as being carcinogenic to humans (Loomis et al. 2013). Due to their small sizes, fine particles can penetrate deep into the lungs and enter the blood. Thus, health-related problems are the primary concern for fine particles, requiring emission regulation. The physical and chemical properties of these particles greatly affect their health effects. Combustion sources are highly heterogenic emission sources; the characteristics of particles and gases vary substantially from one source to another (Flagan and Seinfeld 1988, Ostro et al. 2007). Furthermore, fine particles also cause environmental problems that affect solar radiative forcing, corrode materials and cause impaired visibility (Horvath 1993, Kucera et al. 1995).

Wood is the most commonly used biomass fuel in Nordic countries due to the large forest base, forest industry and relatively easy access to cheap wood for many individuals. Based on the total heat and power production in Finland in 2013, 24% was produced using wood biomass, primarily from by-products of the forest industry (Statistics Finland, 2014), and 4.3% (2011) of the total energy was produced with wood in households (Statistics Finland 2012). Although wood combustion produces less carbon dioxide (CO_2) emissions than fossil fuel combustion and residential wood combustion has a great potential for increasing biomass usage, there is the risk of increased emissions of particles and gases and detrimental air quality effects. Typically, emissions from large-scale heat and power production units are low due to legislative measures, well-controlled combustion processes and flue-gas after-treatment techniques (Sippula 2010). However, emissions from smaller units are often not well controlled, which is due to the use of old appliances, conventional and cheap technology, unoptimized use of appliances and a wide variety of used fuels (Tissari 2008). Residential appliances do not typically have emission limits, which is still the case in many countries. Although there are new, less-polluting appliances that are available, old appliances will remain in use for a long time.

Residential wood combustion is known to be a significant source of particulate matter (McDonald et al. 2000, Johansson et al. 2004, Tissari et al. 2007, Karvosenoja et al. 2008, Brandt et al. 2011, Saarnio et al. 2012) and organic compounds, including polycyclic aromatic hydrocarbons (PAHs) (Schnelle-Kreis et al. 2007, Bari et al. 2011, Elsasser et al. 2012, Crippa et al. 2013). The proportion of PM originating from wood combustion sources has been reported to vary greatly in different locations, for example, 3% in Mediterranean urban background air (Reche et al. 2012), 14% in Central Europe urban background air (Brandt et al. 2011), and up to 66% in Finnish suburban air in winter (Saarnio et al. 2012). Certain types of combustion appliances have been identified to contribute greatly to the total emissions from residential wood combustion (Meyer 2012).

Wood pellets are primarily used in continuously operated combustion appliances. These pellets are generally made of sawdust, cutter chips or other wood industry residues. Pellets have low moisture contents, high energy densities, homogenous sizes and low ash contents. Due to their homogenous features, pellets (when used as fuel) have enabled the development of fully automatic residential-scale combustion systems; the ease of use is essential for these systems. Additionally, pellets can be used in industrial power plants designed for pulverized fuels (Obernberger and Thek 2010). Pellets can also be manufactured from non-traditional raw materials, such as bark, straw, reed canary grass or logging residues, and different raw materials can be mixed to form homogenous pellets. Fine particle emissions from modern pellet appliances are typically fuel derived and contain fine fly ash (Wiinikka et al. 2007, Tissari et al. 2008a, Verma et al. 2011, Schmidl et al. 2011), whereas PM emissions from poor combustion conditions can be almost entirely products of incomplete combustion (Tissari et al. 2008b, Elsasser et al. 2013).

The use of wood in heat and power production is increasing. Part of this increased use will be due to the increase in residential appliances. Thus, it is important to ensure that the change from fossil fuels to renewable fuels, which is a part of the climate policy, will be performed without additional air pollution problems and excess stress on both human health and the environment.

2 AIMS OF THIS STUDY

The focus of the research presented in this thesis was the physical and chemical characterization of fine particle emissions produced via pellet combustion. Furthermore, emissions were compared with various small- and medium-scale residential combustion appliances. The individual studies can be summarized as follows.

- **Paper I** analyzed pellet boiler emissions in different operational situations, including different combustion air settings.
- **Paper II** characterized emissions from continuous combustion and batch combustion for different combustion technologies.
- **Paper III** analyzed the effects of pellet fuel raw materials on PM emissions.
- **Paper IV** compared PM emissions from pellet combustion with those from light fuel oil combustion (small scale) and with the emissions from heating plants fired using wood chips and heavy fuel oil (medium scale).

Furthermore, the PM samples characterized in **Papers II and IV** were used in toxicological studies by Tapanainen et al. (2011, 2012) and Kasurinen et al. (2014). However, the results of these studies are not discussed in this thesis.

3 SCIENTIFIC BACKGROUND

3.1 Fuels

The main components of biomass fuels are carbon (C) (50%), oxygen (O) (42%) and hydrogen (H) (6%). The amount of volatile matter is typically between 70–86 w-% (d.b.) (van Loo and Koppejan, 2008), which is substantially higher than coal (approximately 30–40 w-%) (Vassilev and Vassileva 2009). Freshly cut wood has a high moisture content and must be dried before use. In power plants, the moisture content of wood chips can be up to 50% (Kaivosoja et al. 2013), whereas the moisture content of wood pellets is typically less than 10% (van Loo and Koppejan, 2008). Log woods are most commonly used in households; these woods are not easily used in automatic systems. Compared with pellets, log woods require more storage space and labor for moving from storage to the heating system. Wood chips, which are often used in farms, can be used in automated systems. However, due to their low density, wood chips require plenty of storage space. Other biomass products are also used as energy sources.

3.1.1 Pellet fuels

The pellet manufacturing process includes the following steps. 1) The raw material is dried. 2) The material is milled to reduce the particle size and to homogenize the material. 3) The particles are conditioned via the addition of steam to cover the particles with a thin liquid layer; this process reduces adhesion. 4) The raw material is formed into pellets by being pressed through a die. 5) The pellets are cooled because their temperature increases during the pelletizing process. The diameter of the pellets is typically 6-12 mm (van Loo and Koppejan, 2008) (Figure 1). Classification systems have been created for pellet fuels to ensure the proper quality of pellets that are used in different units. The ENPlus certification, which is applied in many parts of Europe, divides pellets into three different classes according to threshold values for the pellet diameter, length and contents of moisture, ash, nitrogen (N), sulfur

(S) and chlorine (Cl) in the fuel (Table 1) (European Pellet Council 2013). ENPlus also sets requirements for the raw materials that are used in the three different pellet quality classes.

Figure 1. Examples of pellets made from different raw materials: a) commercial wood pellet, b) peat pellet, c) a mixture of pine bark and peat and d) rye straw pellet.

3.2 Combustion

In the ideal combustion of hydrocarbons, carbon (C) and hydrogen (H) react with oxygen (O_2) to generate heat and form both CO_2 and water (H_2O). In real applications, combustion conditions are never ideal. Moreover, fuel and combustion air contain several components that affect the combustion process and emission formation. The combustion of solid fuel in real-life applications always require more air than what is theoretically needed; therefore, the general air-to-fuel ratio (lambda, λ) exceeds 1. In addition, the air-to-fuel ratio varies in different areas of the combustion chamber. Optimal λ values also vary between different combustion appliance types, unit sizes and fuels. For example, in spark-ignited internal combustion engines, λ can be less than 1 (Flagan and Seinfeld 1988). Moreover, in biomass-fired industrial-scale units (rotating grate), λ is approximately 1.3 (5% excess oxygen, O_2) (Sippula et al. 2009a), and in small-scale pellet boilers, λ is approximately 2 (10% O_2) (Tissari et al. 2008a).

Table 1. ENPlus requirements for pellets used for heating purposes (Modified from European Pellet Council 2013).

	Unit	ENplus-A1	ENPlus-A2	EN-B
Diameter	mm	6 or 8	6 or 8	6 or 8
Length	mm	$3.15 \leq L \leq 40$	$3.15 \leq L \leq 40$	$3.15 \leq L \leq 40$
Moisture content	w-%	≤ 10	≤ 10	≤ 10
Ash content	w-%	≤ 0.7	≤ 1.5	≤ 3.0
Mechanical durability	w-%	≥ 97.5	≥ 97.5	≥ 96.5
Fines (<3.15 mm)	w-%	< 1	< 1	< 1
Lower heating value	MJ/kg	$16.5 \leq Q \leq 19$	$16.3 \leq Q \leq 19$	$16 \leq Q \leq 19$
Bulk density	kg/m^3	≥ 600	≥ 600	≥ 600
N content	w-%	≤ 0.3	≤ 0.5	≤ 1.0
S content	w-%	≤ 0.03	≤ 0.03	≤ 0.04
Cl content	w-%	≤ 0.02	≤ 0.02	≤ 0.03
Ash melting behavior	°C	≥ 1200	≥ 1100	≥ 1100
Wood types permitted to be used for wood pellet production		Stem wood and chemically untreated residues from the wood processing industry	Whole trees w/o roots, stem wood, logging residues, bark, and chemically untreated residues from the wood processing industry	Forest, plantation and other virgin wood, chemically untreated residues from the wood processing industry, and chemically untreated used wood

3.2.1 Combustion units

Combustion technologies vary widely based on the different size classes and fuels. Fuels used in heat and power production are generally either solid, gas or liquid. Solid fuel combustion technologies include fixed bed, fluidized bed and pulverized fuel combustion with different variations for specific applications. Fixed bed combustion is often used in residential-scale solid fuel combustion. On the contrary, the combustion of liquid fuels is performed in burners in which the fuel is first sprayed before the combustion.

Combustion processes are well-controlled in large power plants. The processes are optimized for certain types of fuels. Moreover, flue-gas cleaning technologies are commonly used, such as electrostatic precipitators (ESP), to ensure good combustion quality and low emissions. The state-of-the-art combustion technology that is used in residential appliances contains many of the same control techniques that are used in large units. Such appliances can be fueled by pellets, wood chips or wood logs, and the combustion units include automated fuel feeding and automatically controlled air input. With proper control and design and good quality fuel, emissions from residential wood combustion can be low (Wiinikka et al. 2004, Sippula et al. 2007, Tissari et al. 2008a). The present situation of residential combustion in Europe is unfortunately bleak. There are numerous residential appliances with either poor or lacking combustion controls. Moreover, the quality of fuel used in these appliances is typically bad, and the appliance operations are far from optimal.

3.2.2 Continuous pellet combustion

Residential-scale combustion appliances that use solid fuel can be divided into two main categories: batch combustion appliances and continuously fired appliances. Combustion processes in appliances equipped with continuous combustion are generally more precisely controlled than batch combustion appliances. Pellets and wood chips are the most commonly used fuels in continuous combustion appliances in the Nordic countries, whereas wood logs are most often used as fuels in batch combustion appliances.

In pellet appliances, fuel is continuously inserted by feeding from the side, bottom or top, determined by the burner technology (Figure 2). Due to the continuous behavior of the process, which is ensured with logic-controlled fuel and air feeds, both heat release and emission formation are more stable than in batch combustion (van Loo and Koppejan, 2008). To ensure proper combustion conditions, different sensor technologies, such as lambda (λ), carbon monoxide (CO), and temperature controls, can be used for controlling the combustion conditions and adjusting the air and fuel feeds. In pellet stoves, heat is typically transported to the air around the stove via convection, but in pellet boilers, heat is accumulated and transferred to circulated water via a heat exchanger. Modern pellet boilers are nearly as ease to use as oil and gas boilers, which has made pellet systems more attractive for residential use. Oil boiler systems can also be retrofitted to be fueled with pellets by replacing the burner and fuel conveyor system.

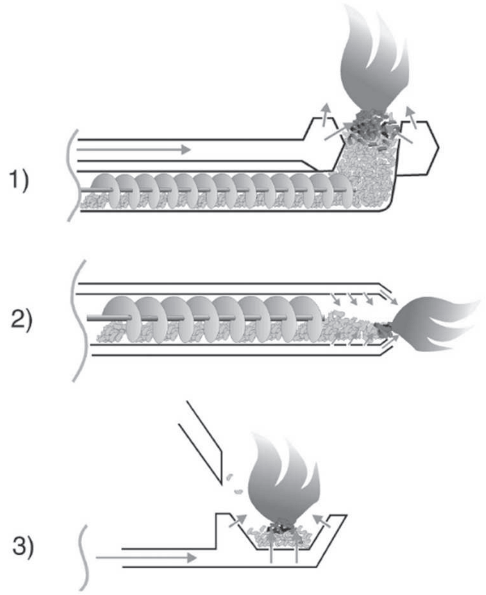


Figure 2. Examples of the most commonly used wood pellet feeding techniques in residential appliances (van Loo and Koppejan, 2008): (1) underfed burner, (2) horizontally fed burner and (3) overfed burner.

3.2.3 Batch combustion

Batch combustion appliances are the most common residential appliances. In batch combustion, a batch of wood is inserted into the appliance and fired. After a certain period of time, typically when the flames burn down, the next batch is added to the appliance. This activity is repeated for a certain period of time, which is based on the appliance type and the required amount of heat. Due to the periodic behavior of the combustion process, heat release and the formation of emissions are not stable. In uncontrolled systems, an addition of a new batch of wood can result in fast pyrolysis of the fuel and in inadequate mixing of gases and oxygen, which leads to incomplete combustion and high emissions (Tissari et al. 2009). Because the behavior of combustion in batch combustion appliances varies significantly with time, designing a properly working appliance can be challenging. In modern batch combustion appliances, the combustion rate is regulated by reducing the amount of combustion air that enters through a grate; a portion of the air is transferred into the upper zone of the combustion chamber as secondary air (Nuutinen et al. 2014). This technique reduces the variations in the batch combustion process.

3.3 Emissions

The emissions from biomass combustion can be divided into two main classes: gaseous and particulate emissions. Particle emissions can be further divided into three main subclasses: organic material, soot and inorganic material. Particulate organic matter (POM) and soot are products of incomplete combustion; their contributions to the total PM emissions can vary significantly depending on the combustion conditions. Inorganic fine fly ash particles are fuel derived. Moreover, because these particles are not products of incomplete combustion, their reduction is not possible by improving combustion efficiency.

3.3.1 Soot

Soot is one of the most important pollutants originating from combustion processes due to its effects on both climate and health. The International Agency for Research on Cancer has recently classified diesel soot as being carcinogenic to humans (IARC 2012). Soot has adverse effects on visibility (Horvath 1993) and is known to be a carrier for PAH species (Richter and Howard 2000, Oster et al. 2011, Laskin et al. 2012, Furuhata et al. 2012). Recent findings regarding the climate effects of soot have highlighted the significance of soot emissions and emission controls (Jakobson 2010, Bond et al. 2013), especially in the Arctic (Stohl et al. 2013). The formation of soot creates the characteristic yellow light in candles; moreover, soot is necessary in boiler flames to obtain good radiative heat transfer (Flagan and Seinfeld, 1998).

Different definitions and terminology are used in the characterization of soot (Petzold et al. 2013). The so-called thermal-optical method is often used in combustion studies to determine the fractions of soot and organic carbon (OC). In this context, soot is often called elemental carbon (EC). On the contrary, black carbon (BC) is used in connection with atmospheric light-absorbing carbonaceous aerosol (Bond et al. 2006). Although EC, BC and soot are often used as equivalents, their definitions are slightly different (Bond et al 2006).

Despite the extensive research over the past decades, soot formation remains a process that is not well understood, especially compared to the formation of inorganic particles (Flagan and Seinfield 1998, Wang 2011). Soot formation is a complex phenomenon in which hydrocarbon chemistry occurs within a flame. Soot has been extensively studied in hydrocarbon flames and in diesel engines; however, few studies have focused on soot emissions from the combustion of solid biomass. According to Richter and Howard (2000), the basic steps for soot formation are as follows. First, the molecular precursors of soot are thought to be heavy PAHs. The growth from small molecules to larger PAHs is thought to involve the addition of C_2, C_3 and some other small units (such as acetylene) to PAH radicals and the reactions among growing aromatic species, such as PAH-PAH radical recombination and addition reactions. The contribution of different types of growth reactions is thought to be fuel dependent. The second phase includes the nucleation or inception of particles from heavy PAH molecules to form nascent soot particles. Third, nascent soot particles grow due to the addition of gas phase species, such as acetylene and PAHs. Next, soot particles agglomerate due to reactive particle-particle collisions. Although the mass remains constant during this process, the particle number decreases in conjunction with an increase in particle size. For longer residence times and under pyrolytic conditions in the postflame zone, polycyclic aromatic compounds undergo functional elimination, cyclization, ring condensation and ring fusion, which is attributed to dehydrogenation and the growth and alignment of polyaromatic layers. This process converts the initially amorphous soot material into an increasingly more graphitic carbon material with a slight decrease in the particle mass. Finally, the oxidation of PAH and soot particles is a process that competes with the formation of the species. Oxidation decreases the mass of PAHs and soot through the formation of CO and CO_2. Oxidation of soot in diffusion flames occurs after the formation process. However, in pre-mixed flames, the formation and oxidation processes occur simultaneously. The main oxidation reactants are OH (most important in fuel-rich flames), O and O_2 (most important in fuel-lean flames) (Richter and Howard, 2000). Because soot formation cannot be avoided in diffusion flames, the oxidation of soot is especially important for controlling soot emissions (Wiinikka and Gebart, 2004, Furuhata et al. 2012). Soot particles oxidize and burn rapidly when they pass through the flame front. However, very fast dilution with cold air may lead to soot emissions despite the presence of oxygen (Flagan and Seinfeld, 1998). Roughly spherical primary soot particles with diameters of 10-50 nm typically form chained agglomerates (Wentzel et al. 2003) (see Figure 3).

Recent studies have suggested that lignin decomposition products play an important role in soot formation from wood combustion (Baeza-Romero et al. 2010). Soot from biomass combustion differs from hydrocarbon soot and contains more oxygenated functionalities, such as o-PAHs, than hydrocarbon soot (Fitzpartick et al. 2007, Baeza-Romero et al. 2010). Many of these compounds can be attributed to the original fuel. Furthermore, the larger observed oxygen contents in biomass emission particles make these particles more hydrophilic and, therefore, more active as cloud condensation nuclei (Picaud et al. 2004), can change the particle optical properties (Mochiad et al. 2004) and can change the potential for causing adverse health effects (Sklorz et al. 2007). Soot has been considered to be a component of particulate matter that absorbs light. However, recent investigations have reported that organic coatings on particles can increase the light absorption efficiency, indicating that organic compounds contribute to the light absorption capabilities of PM (Schnaiter et al. 2005, Shiraiwa et al. 2010, Heringa et al. 2011).

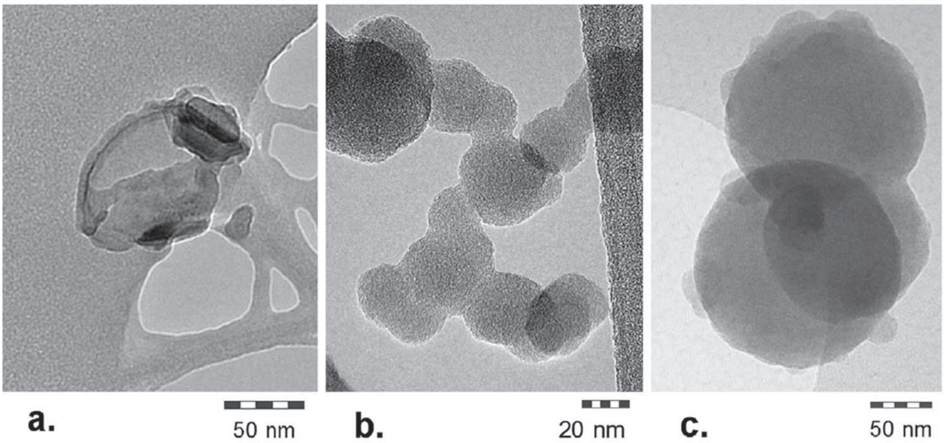


Figure 3. Typical morphologies in a specific combustion system (Transmission emissions microscopy images; Torvela et al. 2014): (a) a typical ash particle, (b) primary particles in a soot agglomerate and (c) particulate organic matter.

3.3.2 Organic emissions

The main components of wood are cellulose, hemi-cellulose and lignin. A complex mixture of volatile organic compounds (VOC) and POM is emitted from wood combustion in both the gaseous and particulate phases (McDonald et al. 2000, Tissari et al. 2007) due to incomplete combustion (Figure 3). The main organic compounds of biomass combustion are monosaccharide derivates from the breakdown of cellulose (Simoneit et al. 1999), which has characteristics that depend on the temperature of the cellulose decomposition (Simoneit 2002). Other important organic components of biomass smoke include alkanes, resin compounds, anhydrous sugars, phenols, lignans, and PAHs (Simoneit et al. 1999, Hays et al. 2011, Orasche et al. 2012, 2013).

Due to their carcinogenicity, PAHs are a well-known group of organic compounds that are contained in combustion emissions (Boström et al. 2002, Tapanainen et al. 2012, Jalava et al. 2012). Residential wood combustion is one of the largest sources of PAHs (Tissari et al. 2007, Hytönen et al. 2009, Bari et al. 2011). PAHs are formed in the oxygen poor area of the flame, which is where polymerization occurs instead of oxidation; the emissions are greatly affected by the combustion efficiency (Johansson et al. 2004, Tissari et al. 2007).

Dilution in the atmosphere and in sampling systems affects the partitioning of semi-volatile organic compounds between the gas phase and particulate phase. Gas-particle partitioning occurs via absorption with an organic solution or adsorption to soot or inorganic particles. When the dilution ratio increases further, a portion of the semi-volatile organic compounds evaporate, which reduces the particle mass (Lipsky and Robinson 2006).

Once in the atmosphere, volatile organic species can contribute to SOA formation (Robinson et al. 2007). Organic compounds go through reversible phase partitioning, deposition and chemical reactions with oxidant species. Organic aerosol becomes more oxygenated during aging, less volatile and more hygroscopic (Jimenez et al. 2009). SOA is formed when volatile species have sufficiently low volatility to partition to the particle phase. Wood combustion, which is an important source of organic aerosols and VOC, has been identified as a source of SOA both in laboratory experiments and in the atmosphere (Grieshop et al. 2009, Heringa et al. 2011, Elsasser et al. 2012).

Traditionally, all light-absorbing material in the atmosphere has been considered soot (or black carbon). However, there is evidence that some organic matter has light-absorbing effects. Therefore, the term "brown carbon" has been suggested for light-absorbing organic matter (Andreae and Gelencsér 2006). Brown carbon interferes with the measurement of black carbon in many situations, especially regarding biomass combustion aerosol measurements.

3.3.3 Fine fly ash particles

Fine fly ash particles from wood combustion are formed from inorganic ash-forming elements in the fuel that volatilize at typical combustion temperatures and form particles when the flue gas cools or via chemical processes in the flue gas; primarily alkali metal chlorides, sulfates and carbonates are formed (e.g. Valmari et al. 1998, Tissari et al. 2007, Sippula et al. 2007). Fine fly ash particles are important not only in industrial-scale combustion but also in continuously operated residential-scale appliances, such as small pellet burners and boilers, where OC and EC particle emissions are low. In woody biomass combustion, the most important released elements include alkali metals (primarily K and Na), S, Cl, P and some heavy metals, such as Zn.

In hot flue gas, volatilized species form very small particles via homogenous nucleation; these particles grow via coagulation and additional condensation of vaporized ash-forming elements. At high temperatures, agglomerated particles may coalescence into dense spheres. However, after combustion, the gases cool below the melting point of the condensed material, the liquid freezes and sintering effectively stops. Torvela et al. (2014) suggested that in Zn rich fuels, ZnO particles from Zn vapor would be the first particles to form, most likely in the oxygen-rich secondary combustion zone, and act as a nucleus for other fine fly ash condensation. ZnO formation is followed by gas-to-particle conversion of alkali sulfates, carbonates and chlorides. Collisions among the solid particles produces chain-like agglomerates (such as those in Figure 3), which are common features of aerosol particles that are produced by vapor nucleation in high-temperature systems (Flagan and Seinfeld, 1988, Torvela et al. 2014).

Alkali metals play an important role in the formation of fine fly ash particles. It has been shown that the concentration of alkali metals in fuels can correlate with the concentrations of alkali metal compounds that are found in the particles (Sippula et al. 2007). However, not only the concentration of ash-forming elements in the fuel but also the release of ash-forming elements affect emissions from different fuels. The release is primarily affected by the fuel bed temperature and the fuel ash chemical composition (Dayton et al. 1995, Baxter et al. 1998, Knudsen et al. 2004, van Lith et al. 2006). Previous studies have shown that higher Cl contents in fuels lead to increased fine particle emissions (Lind et al. 2006, Tissari et al. 2008a); however, in S-rich fuels, alkali metals tend to form alkali sulphates instead of alkali chloride. Alkali sulphates are less volatile and are more likely retained in the bottom ash, which leads to fewer problems on heat exchanger surfaces because these compounds are less sticky (e.g. Lind et al. 2006, Sippula et al. 2008). A fraction of K also reacts with silicates that are present in fuels to form potassium silicates, which are not as volatile as potassium chlorides or sulfates. However, potassium silicates (and other alkali silicates) melt at relatively low temperatures and may cause slagging problems in the fuel bed (Baxter et al. 1998, Khan et al. 2009). The release behavior of ash-forming elements can also be influenced by additives, which have been used to capture alkali metals in the coarse ash fraction. The use of kaolin as an additive has been studied in biomass fuels for inhibiting the formation of corrosive KCl fumes and particles or for decreasing the slag formation by increasing the ash deformation temperature (Steenari et al. 1998, Aho 2001, Davidsson et al. 2007, Khalil et al. 2011). The use of additives in residential appliances has been shown to reduce PM emissions (Tissari et al. 2008a, Sommersacher et al. 2013). For example, the mixing of biomass fuels and peat has been used to reduce gaseous KCl, KCl deposits and fine particle emissions (Kassman et al. 2013, Näzelius et al. 2013, Fagerström et al. 2014).

Laboratory studies of different biomasses conducted in controlled environments have shown that the release of different elements varies greatly with the combustion temperature. At temperatures less than 500 °C, Cl is primarily evaporated (van Lith et al. 2006), although smaller quantities of organically associated K may also be released (van Lith et al. 2008). K and Na are not released in large quantities from fuels for temperatures less than 700 °C (Jensen et al. 2000, van Lith et al. 2008); however, the release of these elements increases sharply between 800 °C and 1150 °C, respectively (van Lith et al. 2008). At temperatures exceeding 800 °C, K interacts with silicates in the ash and affects the release (van Lith et al. 2008). S release has been found to occur in two phases. First, a fraction of S is released at temperatures less than 500 °C, which is due to the decomposition of organic S compounds. At temperatures between 850 °C and 1150 °C, inorganic S is gradually released (van Lith et al. 2006). Some heavy metals, such as Zn and Pb, are also found in biomass fuels (Jones et al. 2014) and vaporize at combustion temperatures exceeding 500 °C (van Lith et al. 2008). The vapor subsequently forms particles. The release increases with increasing combustion temperature (Jimenez et al. 2008, Wiinikka et al. 2013). Some metals behave like alkali metals; their release can be reduced by changing the S/Cl ratio of the fuel (Sippula et al. 2008).

In addition to problems in the atmosphere that are induced by fine particle emissions, inorganic components in biomass fuels are connected with several disadvantages in combustion processes. In residential-scale appliances, fine particles may cause deposition on heat exchangers and slag formation on grates, which disturbs the combustion process (Baxter et al. 1998, Öhman et al. 2004, Lindström et al. 2007, Gilbe et al. 2008). Formation of slag may impair combustion conditions and cause emissions of carbonaceous species or even operational shutdowns. In addition to the aforementioned problems, in fluidized bed combustion, fine fly ash particles may also cause agglomeration of fluidized bed material, heat exchanger fouling and high-temperature corrosion (e.g. Baxter et al. 1998, Khan et al. 2009).

3.3.4 Particle emission factors

Particle emission levels from residential combustion appliances can vary significantly according to the combustion technology, fuel and combustion control. For example, emissions from burners and boilers fueled with wood logs and pellets have been reported to vary between 13 and 23 mg/MJ; the minimum and maximum values are 4.6 and 44 mg/MJ, respectively (Obaidullah et al. 2012). Extremely low PM_1 emissions have also been reported from a prototype gasification combustion pellet burner (2.4 mg/MJ, Nuutinen et al. 2010). In older boiler types and when agricultural biomasses are used, PM emissions can be as high as 2200 mg/MJ for old wood log boilers (Johansson et al. 2004) and 215 mg/MJ for rape straw pellets (Carroll and Finnan 2013). Moreover, some operational inadequacies can further increase the emissions (Schmidl et al. 2011).

Modern automated appliances are designed to function continuously for different power demands, which has decreased the need for startup and shutdown procedures. However, combustion conditions during low load operation are not optimal with respect to the combustion chamber design, leading to increased PM emissions and incomplete combustion conditions (Johansson et al 2004, Tissari et al. 2008a, Boman et al. 2011, Verma et al. 2011, Schmidl et al. 2011). Schmidl et al. (2011) reported that EC emissions increased in low load operation, whereas less fine fly ash were found in PM compared to full load operating conditions. Some studies have also reported that the increase in emissions due to decreased power may also be very small (Schmidl et al. 2011, Johansson et al. 2004).

In batch combustion, particle emissions are dominated by emissions from incomplete combustion, including soot and organic material (Tissari et al. 2007). The formation of these species is influenced by both combustion technology and user behavior (Tissari et al. 2009). In modern batch combustion appliances, these emissions always occur, whereas in automatically operated pellet appliances, especially in large-scale combustion units, emissions originating from incomplete combustion are very low.

3.3.5 Gaseous emissions

In addition to particle emissions, many gaseous compounds are also emitted during combustion. These compounds include CO_2, CO, NO_X, SO_X, and the aforementioned gaseous hydrocarbons. CO_2 is a greenhouse gas that is always released in combustion process despite the combustion quality. Carbon monoxide, CO, is an intermediate product of carbon oxidation to CO_2, and CO formation occurs in fuel-rich regions of the flame. The CO emissions are determined by the oxidation of CO (mixing, temperature and O_2 concentration) and not the formation in the flame. In modern residential appliances, e.g., pellet appliances, CO and hydrocarbon emissions are low (Nussbaumer 2003). CO toxicity is particularly important in household appliances. CO can cause fatal poisoning if released in enclosed spaces (Omaye 2002). Eventually, CO oxidizes to CO_2. However, together with VOCs and NO_X, CO contributes to tropospheric ozone formation.

In biomass combustion, NO_X emissions (NO and NO_2) are formed via several pathways. The most important mechanism in biomass combustion is the formation of NO_X from fuel-N, whereas thermal-NO_X formation does not play a significant role due to the relatively low combustion temperatures (Flagan and Seinfeld, 1998). NO and NO_2 are among of the most important molecules in atmospheric chemistry. NO is rapidly oxidized to NO_2 in the atmosphere, causing acidification in the environment. NO_X in atmosphere is involved in several chemical reactions and contributes to, e.g., in the formation of SOA and tropospheric ozone. Moreover, N_2O is formed during the combustion process. N_2O is a very strong greenhouse gas (Solomon et al. 2007) and takes part in ozone depletion (Ravishankara et al. 2009). NO_X emissions in residential biomass combustion are generally low because both combustion temperatures are low and wood fuels are low in nitrogen; however, NO_X emissions may increase when other types of biomass fuels, such as agricultural biomasses, are used because these fuels have higher N contents (Rabacal et al. 2013).

Sulfur oxides, i.e., SO_2 and SO_3, are formed during the combustion of sulfur-rich fuels; the formation is affected by the S contents of the fuel (Carvalho et al. 2013). Biomass fuels are rich in alkali metals, which bind with S and Cl and prevent the emissions of SO_2 and HCl. Thus, molar ratios of the fuel (K+Na)/(Cl+2S) that exceed one are known to indicate low SO_2 and HCl emissions (Jensen et al. 2001, Sommersacher et al. 2012). SO_X is harmful to both human health and the environment and causes corrosion in materials (Flagan and Seinfeld, 1998). Acidification of forests is the best known effect of SO_X emissions. Moreover, SO_X emissions have been problematic, especially those originating from industrial processes. Sulfur contents in biomass fuels are generally low; therefore, SO_2 emissions are not a major concern (Vassilev et al. 2010).

3.4 Emission reduction in biomass combustion with primary and secondary measures

Several measures have been applied to reduce emissions from combustion processes based on unit sizes. Although similar principles can be used in both residential- and industrial-scale appliances, their usability varies according to the application. The optimization of combustion appliances is often a tradeoff between efficiency and emission control (van Loo and Koppejan 2008). Here, emission control in residential-scale appliances is primarily discussed. The most common primary emission reduction measures include the optimization of air staging, the optimization of combustion chambers, and the modification of fuel (van Loo and Koppejan 2008) by blending different fuel raw materials or by additives (Tissari et al. 2008a).

Air staging can be used for optimizing the combustion process, which reduces emission of both incomplete combustion and NO_X (van Loo and Koppejan, 2008). Air staging has been used in large units for decades to control temperatures in the flame and in the fuel bed. Recently, air staging has also become common in residential combustion appliances, especially in logic-controlled appliances equipped with λ sensors, such as wood chip boilers and pellet boilers. In addition to λ sensors, combustion processes can be further monitored with thermocouples, CO sensors or draught measurements; the data obtained from these monitoring devices can be used for more precise control (Obernberger and Thek, 2010).

In large units, air staging has been primarily applied to reduce NO_x emissions (Khan et al. 2009, Houshfar et al. 2013). In automated residential appliances, similar techniques for controlling combustion and reducing emissions are being used. In batch combustion appliances, air staging is used to improve the combustion quality (Nuutinen et al. 2014). When combustion air is fed in two stages, the primary combustion air flow can be reduced. This slows the gasification of the fuel and creates both a separate zone for the gasification of the fuel and a secondary combustion zone in which combustion gases are efficiently burned out (Tissari 2008, van Loo and Koppejan 2008).

Optimized air staging can also reduce fine fly ash emissions, although the effect of air staging on particle emissions has not been widely studied in residential appliances. Wiinikka and Gebart (2005) found that reducing the primary air flow resulted in lower fine particle emissions, most likely due to lower oxygen concentrations in the fuel bed, which resulted in lower temperatures and lower vaporization of ash elements. Furthermore, feeding combustion air solely through the grate as primary air led to a two-fold increase in particle concentrations. In another study by Wiinikka and Gebart (2004), high air-to-fuel ratios resulted in reduced particle emissions, and increased combustor temperatures resulted in elevated emissions of ash particles. Secondary combustion is especially important in biomass combustion, where emissions from incomplete combustion are formed in the flame; these products are later oxidized in the secondary combustion process (Wiinikka and Gebart 2004, Wiinikka et al. 2007, Fernandes and Costa 2013).

Reducing NO_x emissions with air staging is possible using two different mechanisms. First, by maintaining under-stoichiometric conditions during the primary combustion process, it is possible to create a reducing environment in the primary combustion zone, where HCN and NH_3 are reduced to N_2 instead of being oxidized to NO or NO_2 (van Loo and Koppejan, 2008, Khan et al 2009). Second, because combustion air is distributed between the primary and secondary combustion zones, less combustion air is fed to the primary zone, which decreases the temperature and reduces the formation of thermal-NO_x. However, staged combustion for reducing NO_x emissions may lead to elevated emissions of unburnt species

(Liu et al. 2013). In addition, flue gas recirculation can be applied to prevent slagging, improve mixing and control the temperature (Obernberger and Brunner, 2012). General values for optimal conditions in the primary combustion process have been identified (van Loo and Koppejan 2008, Obernberger and Brunner 2012) to ensure reduced NOx and unburnt compound emissions, i.e., a residence time exceeding 0.5 sec, an excess air ratio less than 1.0 and temperatures of 900–1000 °C.

Several secondary emission reduction techniques have been used in industrial units for reducing emissions of particles and gases, such as NOx, SOx, HCl and PCDD/F (van Loo and Koppejan, 2008). ESP, condensing heat exchangers, catalytic converters, baghouse filters, scrubbers and cyclones can be used to reduce particle emissions (van Loo and Koppejan 2008, Obernberger and Thek 2010). Various secondary emission reduction technologies are under development for residential-scale use (Gröhn et al. 2009, Hukkanen et al. 2012); moreover, several ESPs are already on the market (Obernberger and Mandl 2011). With the current status of residential-scale ESPs, high particle removal efficiencies can be achieved in good combustion conditions; however, these systems seldom function efficiently in variable and high-emission systems, such as batch combustion, where the need for reducing emissions is the greatest (Obernberger and Brunner, 2012).

4 METHODS

Most of the work discussed herein was performed at the Fine Particle and Aerosol Technology laboratory, which is located at the University of Eastern Finland. Some of the experiments in Paper IV were conducted in the field. Particle sampling and collection must be carefully prearranged to cover the wide variety of emissions from residential combustion, the requirements of the measurement instruments and the interactions between the gas and particle phases, which is particularly challenging during the aerosol sample procedure due to changing temperatures and concentrations.

Gas and particle emissions were investigated in this work; the physical and chemical characterization of particle emissions was the primary focus of the investigations. A schematic representation of the measurement system is shown in Figure 4.

4.1 Combustion appliances

Small-scale appliances were used in Papers I–III and partially in Paper IV (Table 2, Figure 5). These appliances are typically used for heating rooms or houses. The masonry heaters used in Paper II heat the environment by natural convection and radiation, whereas heat produced by pellet boilers, oil burners, and larger units is transformed to a fluid through heat exchangers, which is used to transport heat to specific locations.

The pellet boiler used in Papers I, II, III and IV was an Austrian-made, automated fixed-grate pellet boiler with an integrated burner and boiler (Biotech PZ-RL 25 kW). The boiler operates using a top feed (also “overfeed”) principle, in which the pellets are dropped onto the grate from the top (Figure 2). This technique ensures that the fuel feed is accurately controlled and that the danger of back burn from the furnace to the storage tank is nonexistent. However, dropping new fuel on the burning fuel can disturb the flame, resulting in the release of some larger particles (Fiedler 2004). Automated and well-controlled operations result in relatively low emissions of gaseous species and particles, which was described in the previous chapter. In the pellet boiler used in this work, combustion air is led in through separate primary and secondary air inlets. Primary air is inserted from the bottom of the combustion chamber through the grate, and secondary air is inserted in the upper part of the combustion chamber, approximately 10 cm above the grate and through 12 secondary air inlets. The combustion air flows were continuously measured in the experiment system used in this study. The total λ and primary and secondary air flows were used to calculate both the primary lambda (λ_{Pri}) and the secondary lambda (λ_{Sec}).

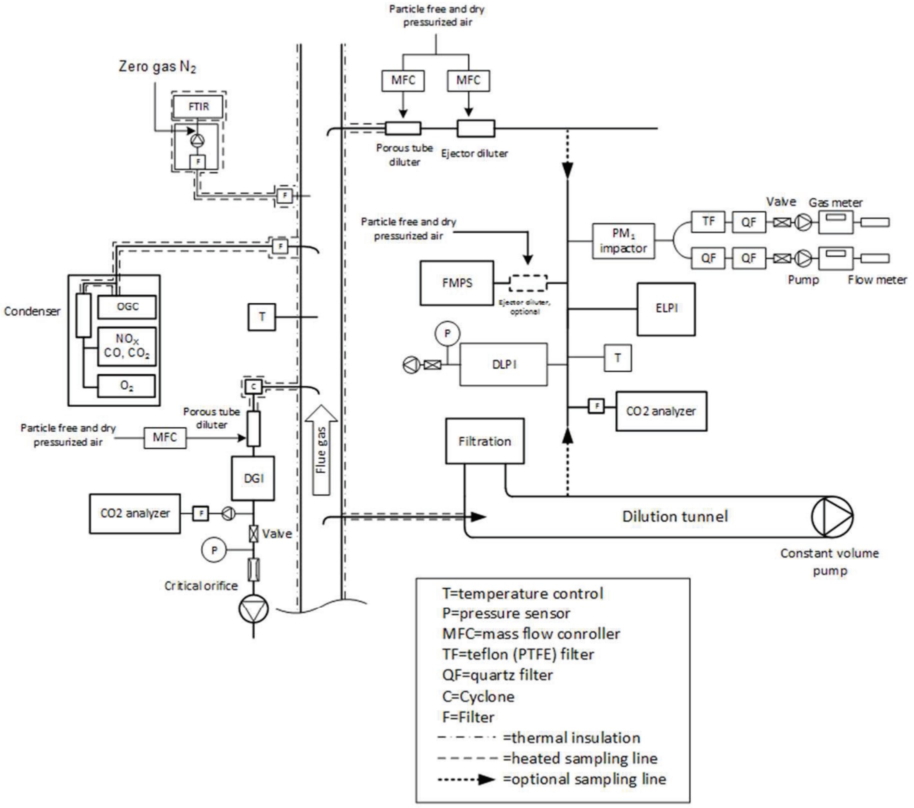


Figure 4. Schematic drawing of the measurement setup.

Conventional masonry heaters are the most common residential combustion appliances for heating individual rooms or houses in Finland. These heaters are typically capable of storing heat for long periods of time with relative steady and low thermal output. Conventional masonry heaters are often made of bricks, soap stone or rock casting material. In these appliances, fuel can be combusted at relatively high burning rates; moreover, heat is stored in the material and released to the surrounding air over a period of several hours (up to 48 h) after the combustion has been stopped (Tissari 2008). Combustion technology in conventional masonry heaters (and in sauna stoves) is rather simple. Wood is inserted on a grate or on the bottom of the combustion chamber; combustion air is primarily introduced through the grate and/or through the door. Flue gases inside the masonry heater first rise and then fall, possibly rising again to ensure a sufficiently long residence time with the heat-storing material (Figure 5). Sauna stoves are operated following a similar principle to conventional masonry heaters. However, sauna stoves are light weight and are designed to rapidly release heat to the surrounding room.

Modern masonry heaters stand out from conventional heaters due to the improvements in the combustion chamber structure and the separation of combustion air into primary and secondary air flows (Figure 5). Secondary combustion air is generally inserted into the upper part of the combustion chamber to improve combustion quality. Additionally, combustion air flow through the grate can be reduced to control the fuel temperature and to prevent excessively rapid devolatilization of the fuel. Reflecting materials can be used in the combustion chamber to increase the temperature and to improve burnout quality. Generally, in modern Finnish masonry heaters, the combustion process exhibits less variability than in conventional heaters. Moreover, both gaseous and particle emissions are lower in modern masonry heaters (Nuutinen et al. 2014). Previous results have indicated that with this technique, the burnout of EC may not be enhanced as efficiently as the other components of incomplete combustion.

A 20 kW light fuel oil burner was used in Paper IV. This burner was equipped with a pressurized atomization system for the fuel, which is commonly used in residential heating systems. The fuel in the light fuel burner was commercial light fuel oil.

Table 2. Explanations of the appliances, fuels and their abbreviations.

	Abbreviations	Explanations	Appliances	Fuels
Paper I	L_{25}	Nominal output, 25 kW	Pellet boiler, 25 kW	Commercial wood pellet
	$L_{12.5}$	Lower output, 12.5 kW		
	L_7	Lower output, 7 kW		
	$Prim_1$	Primary air 29%		
	$Prim_2$	Primary air 18%		
	Sec_1	Secondary air 83%		
	Sec_2	Secondary air 67%		
Paper II	EFC	Efficient combustion	Pellet boiler, 25 kW	Commercial wood pellet, Birch logs
	IBC/34	Improved batch combustion	Modern masonry heater	
	CBC1	Conventional batch combustion, whole cycle	Conventional masonry heater 1	
	CBC2/F	Conventional batch combustion, firing phase	Conventional masonry heater 2	
	CBC3/23	Conventional batch combustion, 2. and 3. batch	Conventional masonry heater 3	
	IEBC/S	Inefficient batch combustion/starting phase	Sauna stove	
Paper III	W1		Pellet boiler, 25 kW	Wood pellet
	W4			Pine bark pellet
	P2			Peat pellet
	WP2			40% Peat – 60 % Pine bark
	WP3			20 % Peat – 80 % Pine bark
	S1			Rye straw
Paper IV	Wood chip	Wood-chip-fired heating plant	10 MW	Wood chip and sawdust
	LFO	Light fuel oil burner	20 kW	Light fuel oil
	HFO	Heavy fuel oil burner	5.2 MW	Heavy fuel oil

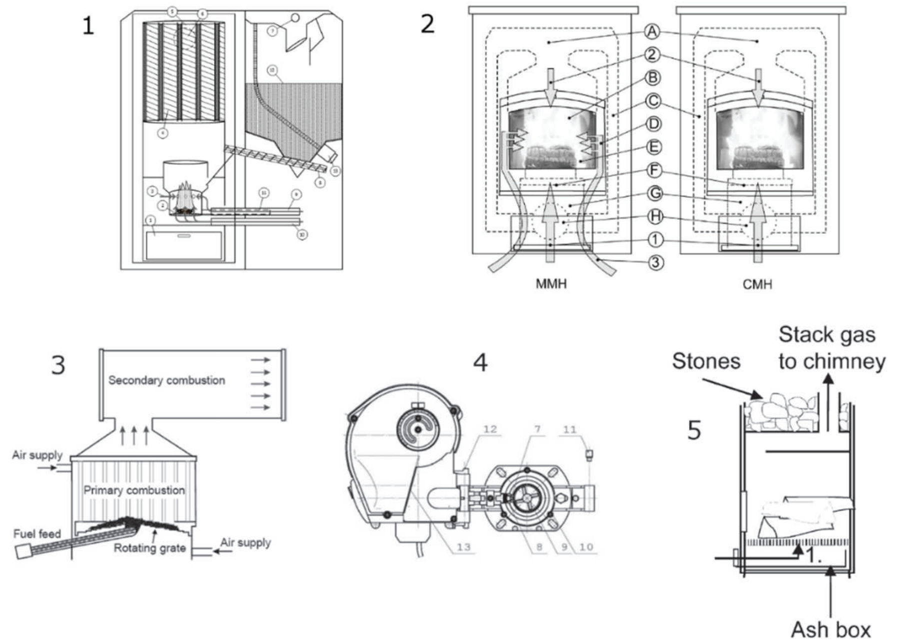


Figure 5. Schematics of the combustion systems (not to scale): a modern pellet boiler (1, Paper I), a modern masonry heater (MMH) and a conventional masonry heater (CMH) (2, Nuutinen et al. 2014), circulating grate combustion technology (3, Sippula et al. 2009b), a light fuel oil burner (4, Oilon Home Ltd) and a sauna stove (5, Tissari et al. 2007).

4.2 Particle measurement and characterization

Sampling is an important part of studying fine particle emissions, especially in small-scale combustion, i.e., where organic compounds can be present in large quantities. Some semivolatile organic species are in present in the gas phase in hot flue gas; however, these species partly condense later on existing particles when the temperature is reduced. Moreover, if samples are obtained from hot flue gas, PM emissions can be substantially underestimated (Nuutinen et al. 2014). In this work, dilution was always used prior to sampling to reduce temperatures, water contents and concentrations and to ensure that the sample better represented the atmospheric conditions.

In Papers I and III (and the secondary dilution system used in Paper II), a partial flow dilution tunnel (built according to ISO 8178–1) was used as a primary dilution system. In this system, a portion of the flue gases are transported from the chimney to the dilution tunnel through a heated sample line (Figure 4). The pressure and flow in the tunnel can be adjusted to control the dilution ratio. The flow was maintained at approximately 650 m^3/h in the tunnel during this work. Laboratory air was used as dilution air in the tunnel; this air was filtered to remove particles, organic compounds and nitrogen oxides.

The primary dilution and particle collection system that was used in Papers II and IV was a porous tube diluter (PRD) (Lyyränen et al. 2004) connected to a Dekati gravimetric impactor (DGI) (Table 3) (Dekati Ltd., Tampere, Finland). The system is described in detail in Ruusunen et al. 2011. The system was designed to be compact and capable of collecting PM for particle characterization and toxicological analyses. The DGI is a five stage cascade impactor (four impaction stages and a back-up filter), which is operated with a 70 lpm flow. The back-up filter and two filter stages were pooled together; these samples were used in the chemical analyses.

The secondary dilution system was a combination of a PRD and an ejector diluter (ED) (Dekati FPS-4000, ejector only) in Paper II, where filter collections were made after the PRD+ED (Table 2). Similar filter collections were made in Papers I and III in the dilution tunnel. Impactors (Dekati PM10 impactor) (Dekati Ltd., Tampere, Finland) were used before the filter collection to remove particles with the size exceeding 1 µm (Figure 5). As described in Sippula et al. 2007 and 2009b, particles were sampled on 47 mm PTFE and quartz plane filters. This collection system was used for the subsequent analysis of organic carbon (OC), elemental carbon (EC) and carbonate carbon (CO_3). Moreover, ICP-MS and IC analyses were performed from the PTFE filters in Papers I and III. OC, EC and CO_3 were analyzed using a thermal-optical method with an analyzer manufactured by Sunset Laboratory Inc. (OR, USA) (Birch and Cary 1996) and based on the National Institute for Occupational Health NIOSH 5040 procedure (NIOSH 1999). OC is typically present in the particle phase as organic matter (OM). The correction factor for changing OC (i.e., the total amount of carbon in OM) to OM varies from 1.2 to 2.5 (Turpin and Lim 2001, Aiken et al. 2008) based on the individual particle properties. For simplicity, OC results are not converted to OM; instead, the results are presented as OC.

Particle mass-size distributions were measured using a 13-stage Dekati low-pressure impactor (DLPI) (Dekati Ltd., Tampere, Finland). The DLPI collects particles with diameters between 30 nm and 10 μm at a 10 lpm flow rate. Aluminum foils were used for impaction plates; the aluminum was greased with a mixture of toluene and Apiezon-L vacuum grease to prevent bouncing. The foils were heated to 105 °C before being weighed to evaporate any extra toluene. Similar foils were used in the pre-cutoff impactors before filter collections.

Particle number-size distributions were measured using two different analyzers, i.e., an electrical low-pressure impactor (ELPI) (Dekati Ltd., Tampere, Finland) and a fast mobility particle sizer (FMPS) (TSI Inc., MN, USA) (based on Tammet et al. 2002). The structure of the ELPI is similar to the DLPI; particles are divided into 13 different size classes using inertial impaction (Keskinen et al. 1992). Additionally, particles are charged in the ELPI with corona charger. When the particles hit the impaction plates, they lose the charge; this charge is measured by the electrometers. The ELPI used herein operates with a 10 lpm flow and measures particles with diameters between 30 nm and 10 μm. When equipped with a filter stage, particles with diameters as small as 7 nm can be observed. Due to its wide measurement range, 1 Hz time resolution and robustness, the ELPI is often used in combustion studies. Particle classification in the FMPS is based on particle electrical mobility. The FMPS is operated with a 10 lpm flow and measures particles with diameters between 5.6 nm and 560 nm (split into 32 size classes). The FMPS also measures with 1 Hz resolution. However, contrary to the ELPI, the FMPS operates at atmospheric pressure. Moreover, the measurements are focused on smaller particles.

Different chemical analyses were performed using the PM_1 samples, including metals, ions and PAHs. ICP-MS was used for analyzing metals, and an IC was used to analyze ions. The PAH analysis included 30 different PAHs. The analyzed PAHs included 16 from the United States Environmental Protection Agency (US EPA 1984) priority pollutant list and 14 from the genotoxic PAHs set by the World Health Organization (WHO-ICPS 1998). A detailed description of the analysis and the analyzed compounds is presented in Paper II. Briefly, PAH compounds were quantified and compared against a mixture of standard compounds. Additionally, deuterated PAH compounds were used as an internal surrogate standard; these compounds were analyzed using a gas chromatography-mass spectrometer (GC-MS, Agilent).

Fuel compositions were analyzed using various methods. For biomass fuels, moisture contents, ash contents, heating values, ash deformation temperatures, and elemental compositions were analyzed. In the analyses of elements, different digestion methods were used, including nitric acid dissolution (also in a microwave oven (EPA3051)) and fluoric acid–nitric acid dissolution. These samples were analyzed with ICP-MS or ICP-AES. A more detailed description of the fuel analyses is presented in Paper III.

4.3 Measurement of gaseous emissions

Gaseous components were primarily measured using two different instruments. An ABB Hartman & Braun gas analyzer system (ABB Cemas Gas Analyzing Rack, ABB Automation GmbH, Germany) was used to continuously measure O_2, CO, CO_2 and NO_X. This system also included a flame ionization detector (FID) for measuring organic gaseous compounds (OGC). Furthermore, a Gasmet DX-4000 (Gasmet Technologies Ltd., Helsinki, Finland), which is based on a Fourier transform infrared (FTIR) spectrometer, was used. This apparatus is capable of measuring H_2O, CO_2, CO, NO, NO_2, N_2O, SO_2, NH_3, CH_4, HCl, HF, and different VOCs, which are especially common in combustion flue gases. The instrument was equipped with an additional O_2 sensor. CO_2 concentrations were also continuously measured in the diluted samples for calculating the dilution ratio (DR) (Figure 4).

Table 3. Particle sampling and measurement systems.

	Paper I	Paper II	Paper III	Paper IV
	Lamberg et al. 2011	Lamberg et al. 2011	Lamberg et al. 2013	Kaivosoja et al. 2013
Source/appliance	Pellet boiler	Pellet boiler, MMH, CMH, and SS	Pellet boiler	Pellet boiler, oil burner, wood chip fired plant, and HFO
Fuel	Commercial softwood pellet	Pellet and birch logs	Pellets of several different raw materials	Pellet, wood chips, LFO, and HFO
Primary sampling system	Partial flow dilution tunnel	PRD[1] PRD+ED[2]	Partial flow dilution tunnel	PRD
Secondary sampling system		Partial flow dilution tunnel[3]+ED[4] PRD+ED+ED[5]		PRD+ED+(ED)
Primary (and secondary) DR	102–124(–1220)	13–26[1], 14–35[2], 88–128[3], 790–810[4], and 280–385[5]	106–187	7.1–65
PM collection	Filter collection (PTFE+quartz) and DLPI	Filter collection (PTFE+quartz), DGI, and DLPI	Filter collection (PTFE+quartz) and DLPI	DGI
PM chemical analyses	OC/EC, anions, and elements	OC/EC, anions, elements, and PAHs	OC/EC, anions, and elements	Anions, elements, and PAHs
Particle number-size distribution	ELPI and FMPS	ELPI	ELPI	

5 RESULTS AND DISCUSSION

5.1 The effect of operating conditions on emissions in a pellet boiler

Modern pellet boilers are capable of using different loads without having to turn the boiler on and off, which has reduced the need for ignitions and shutdowns in real-life operations and has reduced emissions. In typical pellet combustion systems, combustion air flows and fuel inputs are automatically regulated according to needed output powers. Because the combustion chambers and operation are designed to function optimally on nominal loads, changes in fuel and air flows can be expected to affect the combustion conditions at low loads. In Paper I, decreasing the load resulted in slight increases in PM_1 emissions, i.e., from 12.2 mg/MJ to 13.1 and 15.7 mg/MJ when the load decreased from 25 kW to 12.5 kW and 7 kW, respectively. The increase in CO emissions was more evident, i.e., from 64 mg/MJ to 132 and 178 mg/MJ, respectively. These results agree with previous results (Schmindl et al. 2011, Boman et al. 2011). Even small changes in the emissions for different loads may become important with strict emission limits that also account for partial load conditions in type testing. The PM_1 composition revealed that most of the increase in PM_1 emissions was due to increased EC emissions, whereas inorganic emissions exhibited only a slight decrease. Boman et al. (2011) also reported increased PAH emissions for low loads. Interestingly, Figure 6 shows that the PM_1 chemical profile was very similar for low load (L_7), in reduced secondary air (Sec_2) and from modern batch combustion, although the PM_1 emissions exhibited some variability. Increased emissions for low loads were most likely due to higher air-to-fuel ratios in the pellet boiler, especially in the primary combustion zone. Excess air in the fuel bed and in the combustion chamber can reduce the temperatures in the combustion chamber and weaken the oxidation of combustion gases (Gungor 2010). Furthermore, secondary air may lose its capability of penetrating the primary combustion gases, which further reduces oxidation (Koksal and Hamdullahpur 2004). Overall, the emissions for low load conditions remained substantially lower than the emissions from batch combustion in Paper II.

In the experiments where different air settings were investigated, decreasing the secondary air (while keeping the total lambda roughly constant) increased incomplete combustion emissions, especially CO in the gaseous phase and EC in the particle phase. With the lowest secondary air inputs, i.e., where the input was decreased by 33% from the normal setting, the PM_1 emission was 29 mg/MJ, which was approximately 2.4-times higher than when operated with the factory settings; an increase in CO emissions was even more substantial. The decrease in the secondary air flow inputs were 17% and 33%, and their effect on both particle and gas phase emissions were substantial, indicating that even rather small changes in combustion settings can lead to significantly increased emissions.

Reducing the amount of primary air through the grate resulted in lower PM_1 and CO emissions. The primary air was reduced from 174 lpm to 50 lpm and 15 lpm. However, even with such large primary air reductions, the PM_1 emissions were 5.4 mg/MJ and 3.1 mg/MJ, respectively. The decrease in PM_1 emissions is related reductions in both EC emissions and alkali metals. The decrease in PM_1 emissions from 12.2 mg/MJ to 3.1 mg/MJ indicates a considerable emission reduction potential for optimized staged combustion. However, in the context of reducing emissions, the amount of primary air cannot be reduced below certain point without sacrificing the efficiency of the boiler. In the present work, output power of the boiler was not continuously measured; instead, the load with reduced primary air settings was estimated using the total air flow to predict that the output power decreased from 25 kW to 19 kW and 17 kW. However, by redesigning the grate and combustion chamber, it is possible to maintain low primary λ while simultaneously producing the desired amount of heat. In the boiler used herein, the secondary air inlets were relatively close to the grate; therefore, it is possible that secondary air could have created a back flow and was consequentially involved in primary combustion. There were no tools available to study this behavior in more detail. However, the very low primary λ indicates that there may have been additional combustion air in the primary combustion zone, which could have resulted either from leaks or back flow from the secondary air input.

Particle emissions originating from incomplete combustion, especially EC in Paper I, and K and SO_4 originating from the fuel exhibited large contributions to the total PM_1 emissions. When the combustion conditions deteriorated, EC became the most prominent component contributing to the PM_1 emissions; only a slight and insignificant increase in OC emissions occurred. The increased PM_1 emissions through increased EC emissions were similar for partial loads and when secondary air was reduced (Figure 6 and 7). However, for nominal load conditions, the EC emissions were already low; further reductions in EC emissions did not play an important role in reducing the total emissions. Therefore, reducing PM_1 emissions using reduced primary air inputs was largely related to the decreased K and SO_4 emissions. Temperatures on the grate or on the fuel bed were not measured; however, the reduced air flow through the fuel bed may have resulted in reducing conditions and lower fuel bed temperatures, which suppressed the release of alkali metals. Previous results by Wiinikka and Gebart (2005) support these findings. However, in other types of appliances, a considerable increase in primary air caused lower volatilization of inorganic species due to the lower temperatures in the fuel bed (Obernberger and Brunner 2012). Air staging was also used for controlling NO_X emissions; however, in the present system, no effect was observed because the combustion chamber geometry was likely not ideal for reducing NO_X. The primary and secondary combustion zones were not properly separated to ensure both sufficient residence time and the presence of a reduction zone between the combustion zones, which would enable the reduction of NO_X to N_2.

Both the amounts and distributions of primary and secondary air were varied in the experiments, including the partial load tests and the air reduction tests. Various parameters and correlations were determined based on these experiments. These results revealed that the ratio of primary and secondary combustion lambdas (λ_{Pri} / λ_{Sec}) was more important than combustion air flow alone. Figure 8 highlights the correlations between λ_{Pri} / λ_{Sec} and emissions of CO, PM_1, K and EC.

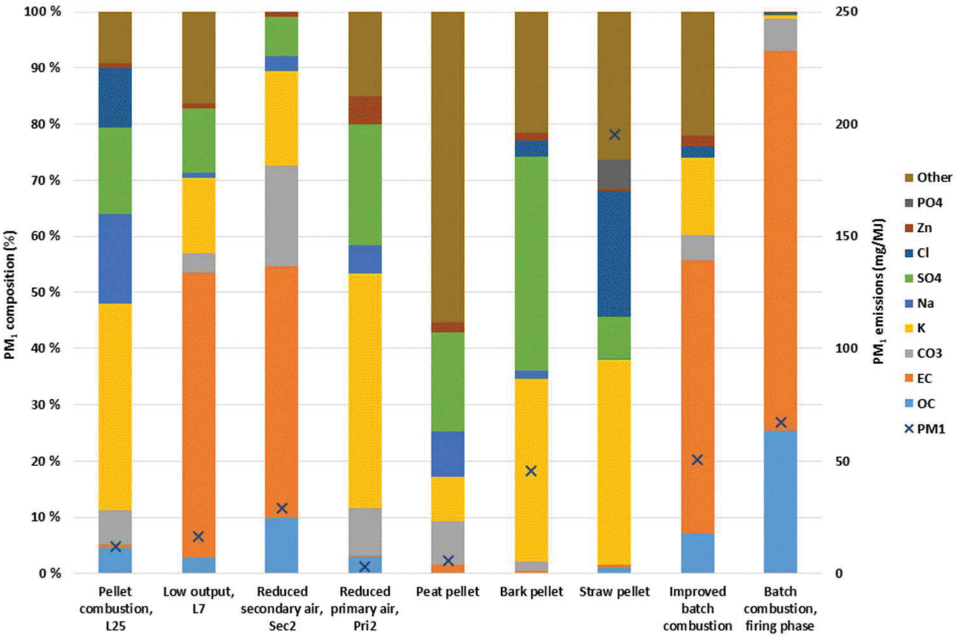


Figure 6. PM1 emissions and compositions in selected experiments.

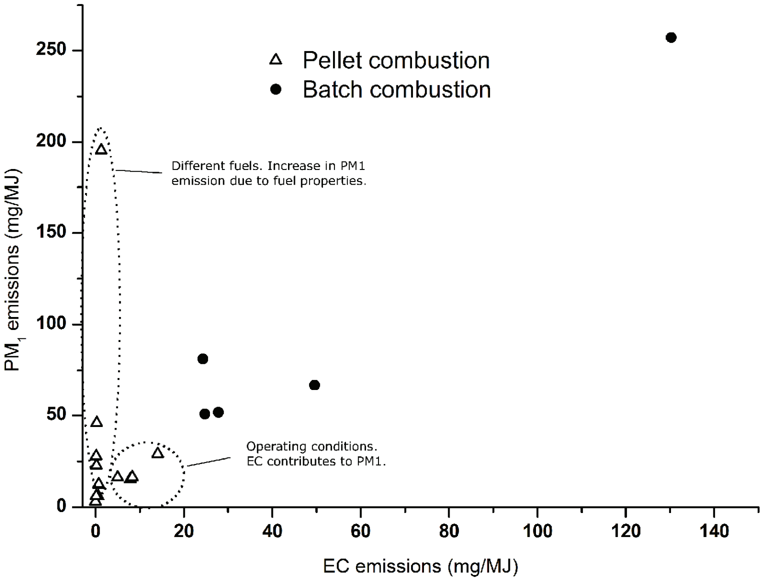


Figure 7. Correlations between EC and PM1 emissions in different experiments.

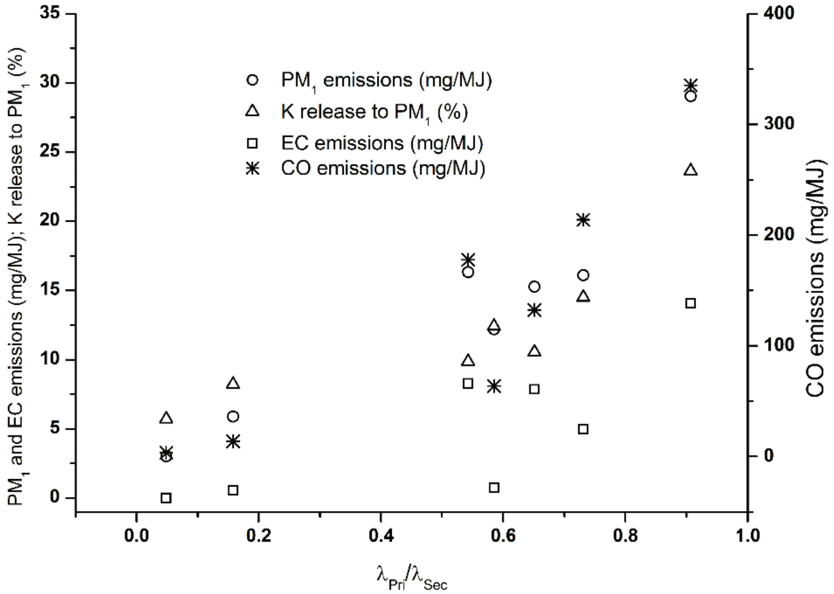


Figure 8. Correlations between $\lambda_{Pri}/\lambda_{Sec}$ and the emissions of PM_1, EC and CO (mg/MJ) and the release of K to PM_1 (%).

5.2 Emissions from a residential pellet boiler compared to batch combustion appliances

Particle emissions from batch combustion appliances contain considerable amounts of EC and OC that originate from incomplete combustion. Furthermore, particle emissions and particle characteristics were found to vary significantly between different combustion appliances and combustion conditions. PM_1 emissions from the studied pellet boiler (Paper II) were 19.7 mg/MJ and primarily composed of inorganic species. The highest PM_1 emissions were measured from the starting phase of a sauna stove (257 mg/MJ). Combined with the firing phase in conventional batch combustion (CBC2 in Table 2), the PM_1 emissions from these two conditions were almost entirely composed of EC and OC, whereas the emissions of particle phase inorganics were low (Figure 6). CO emissions were 5 to 50 times higher in the studied batch combustion appliances than in the pellet boiler, although the air-staging technology in the modern masonry heater resulted in lower CO emissions than in the batch conventional combustion devices used in Paper II. However, the effect of improved combustion technology was not as evident in the PM_1 emissions as in the CO emissions. The most significant difference in emissions between the different combustion appliances and combustion conditions were found in the particulate PAH emissions (Figure 9; Paper II: Table 7). The starting phase of a sauna stove produced the highest PAH emissions, whereas the studied pellet boiler produced the lowest PAH emissions. The PAH emissions behaved in a similar manner to the emissions of a few other compounds, such as OGC; however, PAH emissions were found to be the most sensitive compound to combustion conditions. As a result, the combustion technology affected the PAH emissions more than PM_1 and CO emissions. Toxicological studies (Jalava et al. 2010, Oh et al. 2011, Tapanainen et al. 2012) have shown that the amount of PAH in PM can correlate with the toxicology of the PM_1; therefore, there may be a direct relationship between combustion conditions and health effects.

A direct comparison between the different batch combustion appliances is not straight forward based on the results presented in this thesis due to the differences in the appliances and combustion situations. However, secondary air, or staged combustion, is an important component of controlling emissions in both automated and batch combustion appliances. Old-fashioned appliances are equipped with only one combustion air input or air is led into the system in an uncontrolled manner (typically through the grate and/or the door). Applying automation and fan-assisted combustion air inputs may further improve the combustion quality and reduce the harmful emissions generated in incomplete combustion. Batch combustion is naturally highly variable compared with continuous combustion, such as pellet boilers, making the optimization of the process more complex. In Finnish masonry heaters, such as those used in this work, combustion air input is unforced. This condition most likely leads to situations where combustion air flows are not sufficient for all conditions. Moreover, by maintaining flows that are suitable in some conditions leads to too much air flow for other combustion conditions. More precise combustion air controls would lead to reduced emissions.

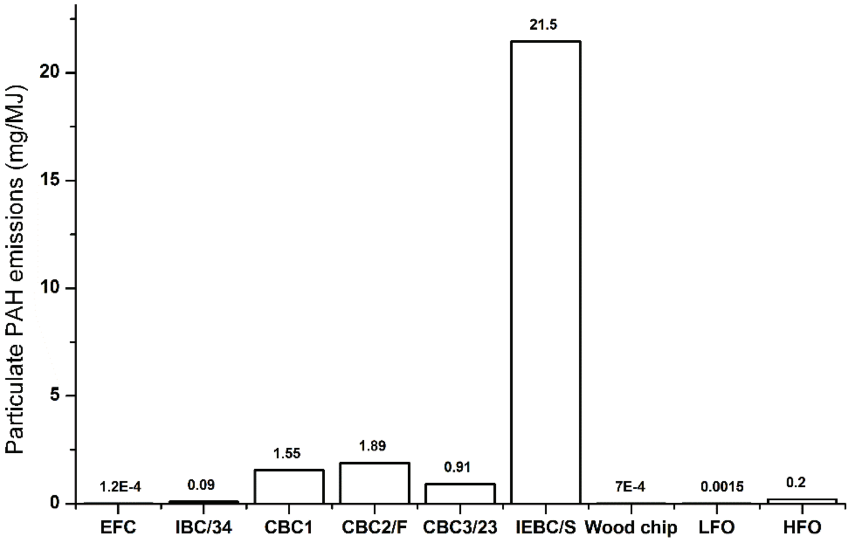


Figure 9. Particulate PAH emissions from different combustion sources.

5.3 Emissions from different pellet raw materials

PM_1 emissions from different pellet materials varied substantially, ranging from 5.1 mg/MJ (for peat pellet) to 195 mg/MJ (for rye straw pellet) (Figure 6). Generally, peat pellets produced the lowest PM_1 emissions and were found to decrease PM_1 emissions when mixed with woody biomass. PM_1 emissions from different pellet raw materials were primarily composed of K, SO_4 and Cl. Significant amounts of PO_4 were observed in the PM_1 emissions from straw pellets (Figure 6). The highest PM_1 emissions were measured for straw pellets; the fuel characteristics of straw pellets are substantially different than the other studied pellet fuels. Some fuel properties, such as the contents of K+Na+Cl and K correlated with PM_1 emissions, and the (K+Na)*2Cl/S molar ratio in the fuels correlated with the sum of K and Na in PM_1. These indicate that these elements in the studied fuels directly affected the formation of PM_1. For example, bark contains relatively high amounts of K and Na; therefore, the use of bark in fuels (for example in forest residues or tree including bark) increases particle emissions.

Two independent factors, i.e., the fuel Si content and the fuel Cl/S ratio, affected the release of ash-forming elements and PM_1 emissions. Si forms alkali metal silicates with alkali metals, which are less volatile than alkali metals chlorides and sulfates; these compounds are more readily maintained in the bottom ash, suppressing their release (Knudsen et al. 2004). Previous studies have also reported that Cl increases the release of alkali metals (Knudsen et al. 2004, Lind et al. 2006), but there are other studies that have supported the finding that S may decrease the release of alkali metals, especially in Cl-rich fuels (Lind et al. 2006, Sippula et al. 2008). Because peat contains more Si and S than woody biomass, the use of peat as fuel to decrease PM_1 emissions can be due to either of these two processes, or a combination the two. However, based on the results, it was not possible to define which process (or if a combination of the two processes) caused the decreased PM_1 emissions. Although Si prevents the release of alkali metals by forming alkali metal silicates, these alkali silicates decrease the ash melting temperature and can create problems in the usability of the fuel by producing ash melt on the grate.

Pellet raw materials did not have a significant effect on gaseous emissions originating from incomplete combustion. However, some operational problems, primarily due to ash melt formation on the grate, disturbed combustion air flows and increased the CO and OGC emissions. Both the CO and OGC emissions were lower when peat-wood mixtures were used than with woody biomass pellets; therefore, the addition of peat to woody biomass improved the combustion conditions. Peat and straw produced the highest NO_X emissions; the addition of peat to woody raw materials increased the NO_X emissions. The highest SO_2 emissions were also measured in peat pellet combustion. Gaseous emissions originating from fuel quality, i.e., NO_X and SO_2, were directly affected by the pellet fuel properties. Straw pellets were the only fuels to create notable HCl emissions. The fuel (K+Na)/(Cl+2S) molar ratio was found to be a good indicator of SO_2 and HCl emissions (Jensen et al. 2001, Sommersacher et al. 2012).

The use of peat fuel is not straight forward in residential combustion for various reasons. Peat was found to decrease the PM_1 and CO emissions when mixed in pellets with woody biomasses; however, peat also increased the gaseous NO_x and SO_2 emissions. Additionally, peat increased the fuel ash content, which can create problems, especially in residential appliances that are designed for low-ash content fuels. Furthermore, peat is not a renewable fuel. The use of peat may be an acceptable additive if small quantities of peat resulted in notable decreases in emissions, which may provide more possibilities for using alternative pellet raw materials in residential-scale appliances. Moreover, previous studies have shown that peat has contributed to rising CO_2 concentrations in the atmosphere and perishing natural ecosystems. The studied wood-peat mixtures contained relatively large (up to 40%) fractions of peat; no systematic analysis was performed for different quantities of peat mixed with woody biomass. Tests with mixtures of peat and woody biomass using reduced amounts of peat are needed to better evaluate the use of peat as an additive for reducing emissions. Yet, peat additives could improve the usability of high alkali content biomass fuels in residential-scale appliances.

The PM_1 emission factors from straw pellets were as high as the emissions from incomplete batch combustion (Figures 6 and 7). Additionally, the PM_1 emissions factors from bark pellets were similar to improved batch combustion, although the particle composition was different. The PM_1 emissions from peat combustion were similar to the PM_1 emissions in optimized pellet boiler emissions when commercial pellet fuel was used (Paper I). Consequently, the use of such fuels in residential pellet combustion may lead to PM_1 emissions that are similar to those from batch combustion. Moreover, despite the lower emissions originating from incomplete combustion, the use of modern combustion technology may not lead to lower emissions. Thus, the utilization of the studied alternative pellet raw materials requires flue gas after-treatment systems. Moreover, based on the current combustion technologies that are available on the market, it is advisable to use these types of fuels in industrial-scale units, i.e., which apply flue gas after-treatment procedures; therefore, excessive particle emissions can be avoided.

5.4 Comparison of renewable and fossil fuels in small and medium scale

The PM_1 emissions (0.1 mg/MJ) from a 20 kW light fuel oil (LFO) boiler were substantially lower than those from the studied pellet boiler; these emissions consisted of EC and SO_4 (Paper IV), which is typical for this appliance type (Hays et al. 2008). Moreover, the CO emissions were low (below the detection limit of our analyzer), and the NO_x emissions were nearly the same as those produced by the studied pellet boiler. Previous work has suggested that replacing fossil fuels in residential combustion with biomass fuels can lead to increased particle and gaseous emissions (Johansson et al. 2004); the results presented herein support this finding.

The emissions from industrial-scale heat production unit fueled with wood chips were found to be low due to efficient secondary emission reduction measures, which resulted in emissions that were slightly higher than from LFO but substantially lower than from the studied pellet boiler.

Energy power plants with a size approximately 10 MW are part of decentralized heat production and produce heat for district heating; these power plants are occasionally connected to a specific industrial process. In this work, the PM emissions from wood-chip-fired power plant before the ESP were high; however, after the ESP, particles were effectively removed. However, in operational situations in which the ESP is not functioning properly, PM emissions can be momentarily up to several hundreds of mg/MJ. Similar to the pellet boiler emissions, the PM_1 emissions were primarily composed K and SO_4; the emissions from incomplete combustion were low. Although the PM_1 emissions were lower, the PAH emissions were slightly higher than from the pellet boiler. This result is surprising because the process in industrial-scale operations is very well controlled and equipped with flue gas after-treatment measures.

Heavy-fuel-oil-fired (HFO) burners are typically used in industrial processes and in district heating for producing heat during peak hours and days. Due to very different fuel characteristics, previous studies have shown that HFO emissions were found to be substantially different than wood chip and LFO combustion emissions; however, these emissions exhibit a few similarities, e.g., the large SO_4 fraction (England et al. 2007, Sippula et al. 2009a). The PM_1 emissions from the studied HFO burner were 20 mg/MJ, which was similar to that of the pellet boiler. SO_4 was identified as the most abundant compound in the particles. A large fraction of the PM_1 was unidentified; however, this fraction likely consisted EC, OC (England et al. 2007, Sippula et al. 2009a) and particle-bound water (Moldanová et al. 2009). Furthermore, some heavy metals were identified; vanadium was the most prevalent. Furthermore, the PAH emissions were even higher than from improved batch combustion (Figure 9). Additionally, the NO_X emissions were higher than from the combustion of stem wood (logs or pellets; Figure 13), whereas the SO_2 emissions derived from the high sulfur contents in the fuels were higher than from any other studied case.

An overall comparison and evaluation of the emissions originating from different heat production systems is very cumbersome. On one hand, bioenergy should be favored to reduce the use of fossil fuels and the production of CO_2 emissions. On the other hand, both gaseous and particle emissions from biomass combustion in residential appliances are larger than from LFO combustion (Paper IV, Johansson et al. 2004). Some emissions, such as SO_2 and NO_X, can be significantly higher in fossil fuel combustion, especially when heavy fuel oils are used. It was also shown in Paper IV that the PAH emissions from wood pellet and wood chip combustion were lower than from the combustion of light and heavy fuel oils. Present legislation for PM emissions are based on particle mass; even though the composition has been linked to the harmfulness of PM, the PM composition is not included in these regulations (Becker et al. 2005, Sklorz et al. 2007, Jalava et al. 2007, Tapanainen et al. 2012).

5.5 Additional examination of the particle emissions

5.5.1 Composition of PM_1 emissions in different combustion experiments

EC and OC constituted a significant fraction of the PM_1 emissions from batch combustion appliances and from the studied pellet boiler when combustion conditions were not optimal (Figure 6). OC was primarily present in the PM_1

emissions from batch combustion appliances, especially when the combustion conditions were extremely poor. Although the amount of OC from batch combustion decreased when the combustion conditions were improved, it was more challenging to reduce the EC emissions (Figures 6 and 7). This behavior was evident in both batch combustion appliances and in pellet combustion. In Paper II, two similar combustion appliances were studied; one appliance represented conventional technology, and the other appliance represented modern technology. The use of modern technology substantially affected the CO, OGC and PAH emissions, but the EC emissions were the same from both appliance types. This behavior in batch combustion was recently reported by Nuutinen et al. 2014. Nevertheless, emissions originating from incomplete combustion can be affected by further optimizing combustion technology. Similar to batch combustion, EC emissions were substantial from the studied pellet boiler with low loads and with reduced secondary air; the PM_1 emissions were increased almost entirely due to increased EC emissions (Figures 6 and 7). Both decreased temperatures and less efficient mixtures of secondary air and combustible gases most likely led to the reduced oxidation of EC and the increased emissions. Similar behavior was also reported by Schmindl et al. (2011) using a pellet boiler under non-optimal conditions. The awareness and importance of EC emissions has recently increased, especially in Nordic countries because EC — in addition to direct climate warming effect — can accelerate the melting of Arctic ice if deposited on the surface of the ice (Bond et al. 2013, Meinander et al. 2013, Jiao et al. 2014).

Paper III presented very different PM_1 emissions from various pellet raw materials. However, the PM composition was found to be very similar in the different fuels despite the different PM_1 emissions (Figure 10). The share of K in the PM_1 emissions was approximately 30% in more than half of the experiments and between 10% and 20% for the other fuels. The proportion of SO_4 varied slightly more, i.e., from 15%–40%, with an average of approximately 20% (excluding the straw pellets). Furthermore, the share of Cl was rather constant, varying from a few percent to 15% (exceeding 20% for straw). If OC, EC and CO_3 were excluded (not shown), K and Na accounted for approximately 30–35% of the PM_1 emissions (varying from 20% to 45%). Similarly, SO_4, Cl and NO_3 accounted for 20%–50% of the PM_1 emissions. PO_4 was important only in PM_1 samples originating from straw pellet combustion (Paper III, Table 6). Based on all of the experiments presented in this work, K represents approximately 20–40% of the total inorganic PM emissions (excluding the two poorest batch combustion cases in Paper II) when the carbonaceous components (OC, EC and CO_3) were excluded from the analysis.

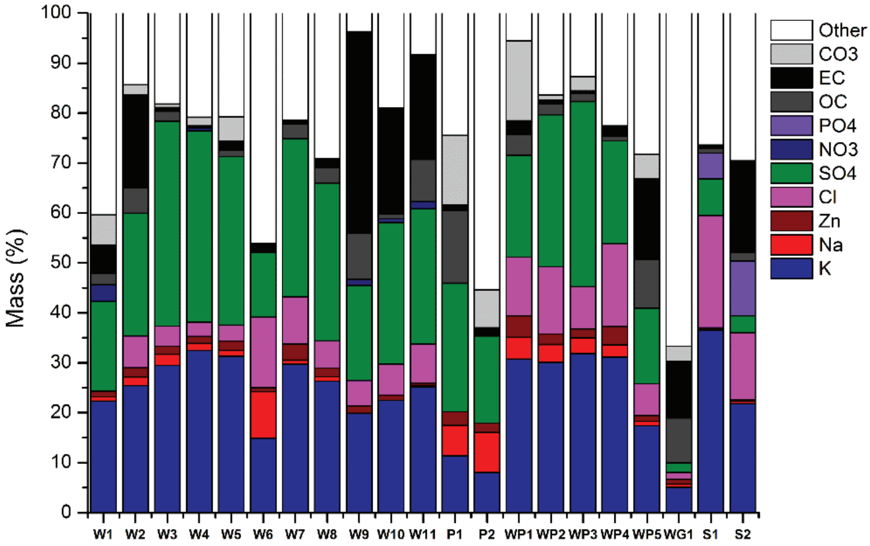


Figure 10. PM_1 compositions for the experiments with different pellet fuels.

5.5.2 Particle number emissions and particle size

Particle number emissions from residential biomass combustion are generally high with smaller particles compared to industrial-scale biomass boilers. The aerodynamic diameters were typically less than 1 µm (Figure 11). Notable amounts of particles with diameters exceeding 1 µm may occur only in very poor combustion conditions and in large appliances.

Batch-wise combustion is naturally highly variable and particle number emissions and particle sizes vary over time. Variation in measured emissions is also present in batch-wise combustion processes from one experiment to another. Thus, identification of uncertainties in limited number of experiments is challenging. Moreover, pellet combustion generated stable number of particles throughout the combustion process compared with batch combustion processes; however, the reduction of secondary air and lower load conditions also made the pellet combustion process less stable (Appendix I: Figure 1). Ash particles are of special importance in biomass combustion; their number emissions are high. Some ash species formed seed particles, but the other condensing species condensed on existing particles rather than forming new particles through nucleation. Previous work has suggested that ZnO may act as a nucleus in fine fly ash particles (Torvela et al. 2014). The particle number emissions were not correlated with combustion conditions or PM emissions, which has been reported also in previous studies (Johansson et al. 2004, Tissari et al. 2008b). Moreover, the particle number emissions were not correlated with the fuel ash content when different biomass fuels were used (Paper III). Although the number emissions were not related to the combustion conditions, the particle sizes (GMDs) increased with increasing PM_1 emissions.

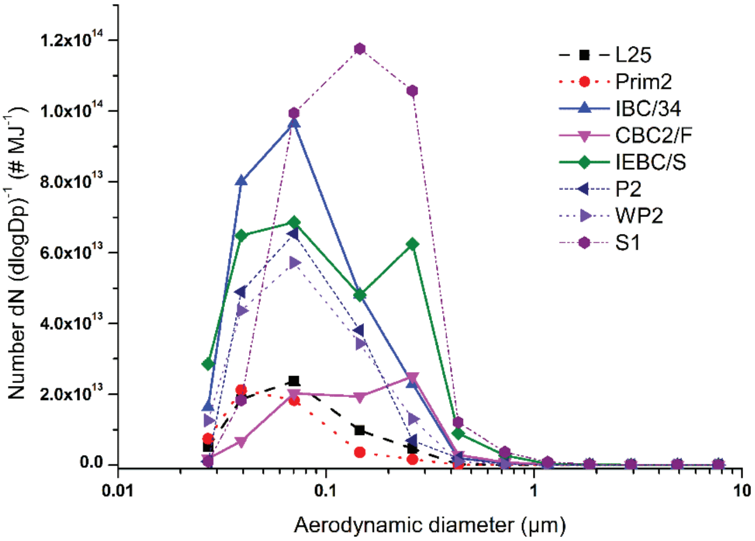
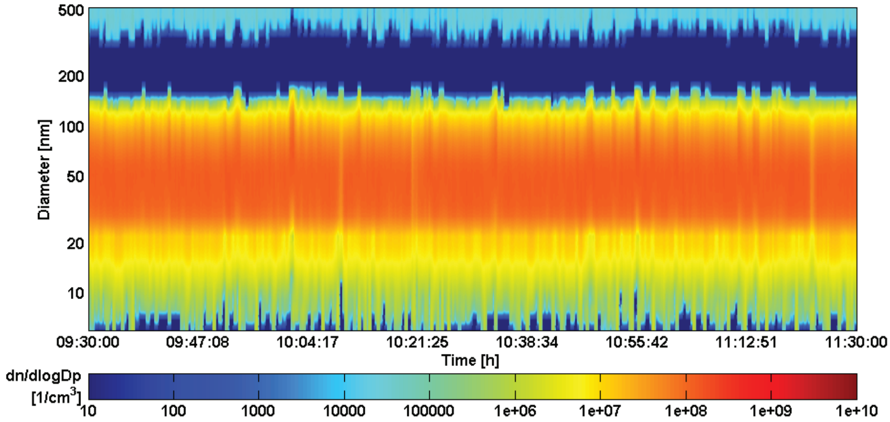


Figure 11. Number-size distribution for different experiments as measured with the ELPI.



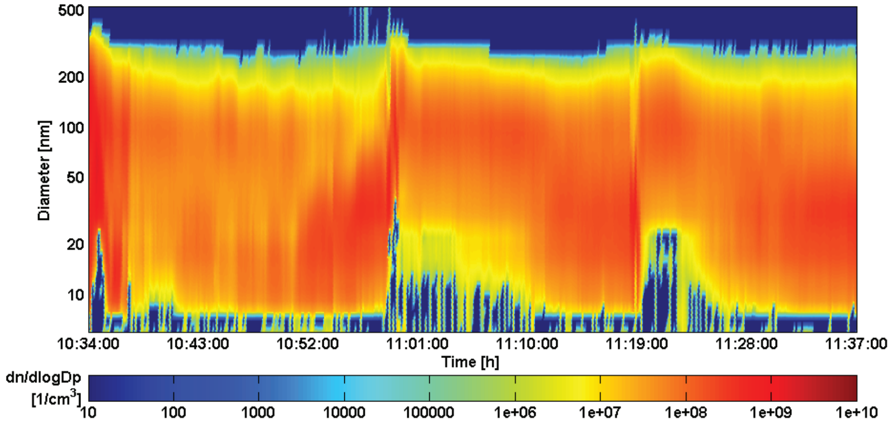


Figure 12. Particle number-size distributions for the pellet boiler with nominal output (L_{25}, top) and for the conventional masonry heater (CBC3, bottom).

5.7 Emissions with respect to emission regulations

Currently, there are no PM emission limits for residential combustion in Finland; however, there is ongoing work devoted to creating a Europe-wide (Ecodesign Framework Directive 2009/125/EC, Lot 15: Solid fuel small combustion installations; Lot 20: Local space heating products) emission limit for residential wood combustion. These regulations will also affect the policies in Finland. Currently, units larger than 1 MW have emission limits in Finland that contain PM regulations (Valtioneuvoston asetus 2013). However, emission limits for residential wood combustion are already applied in many parts of Europe.

Most of the standard measurements are performed with a so-called hot filter sampling, where particles are collected in a hot flue gas onto a hot filter. This technique prevents the collection of most organic phase compounds, which condense first when the flue gas cools to the ambient air temperature and subsequently contribute to primary PM emissions in real-life situations (Lipsky and Robinson 2006). Thus, particles collected from diluted and cooled sample gas are typically desired because they better reflect the conditions in ambient air. Dilution is also required for online particle measurement devices. The dilution tunnel method is used in standard measurements in Norway; however, different operational practices make a comparison with this work even more challenging (Norwegian standard 1994). Despite the differences in measurement methods and their possible effects on emissions, the emission limits form a baseline for emission comparisons. In addition, total suspended particles are measured using standard techniques, whereas PM_1 (also PM_{10} with the DLPI) was sampled in this work. PM_1 was selected because these particles are generated through gas phase processes in the combustion process and cover the main mode of PM emitted from residential combustion.

Pellet appliances typically incorporate modern combustion technology with low emissions. The NO_X emissions from residential appliances are fuel derived, and the combustion technology does not have a major effect on the emissions (Rabacal et al. 2013). There are technological options available to decrease NO_X emissions; however, these options are not yet common in residential-scale appliances. In this work, the NO_X emissions from batch combustion were barely below the limits proposed in the new Ecodesign draft (2009/125/EC, draft Jan 2014 for local space heaters). Moreover, the emissions are also below the emission limit when commercial wood pellets and other pellets that are primarily composed of stem wood were used (Figure 13). When the pellets contained more bark (containing N), such as in logging residues, the proposed Ecodesign NO_X limits were exceeded. The use of peat similarly increased the NO_X emissions above the limit.

The CO emission limits in the Ecodesign proposal have been separated for different appliance types. In the studied pellet boiler, CO emissions were below the emissions limit for most of the tested fuels. Moreover, for mixtures of wood and peat, the emissions were well below the regulations (Figure 13). However, when the combustion conditions were not optimal, the CO emissions may increase, even in automated combustion appliances. This finding was observed with low loads, where the CO emissions slightly exceeded the proposed limit even with the lowest tested load (Figure 13). In the draft of the upcoming standard for biomass boiler testing (Directive 2009/125/EC, Lot 15), partial load tests are also considered, which will most likely lead to increased awareness and to improved appliance designed for handling partial loads.

In Paper II, improved batch combustion with air staging and well-operating conventional batch combustion without air staging emitted less CO than the Ecodesign emission limits, both during the specific combustion conditions and the combustion cycles (Paper II, Table 4). However, the CO emissions from the studied sauna stove with simple combustion technology substantially exceeded the emission limits for CO.

A comparison of PM emissions to the proposed emission limits is more complicated than comparing gaseous emissions due to the previously described sampling issues. Based on current knowledge, it is believed that the effect of different sampling methods on the PM results is smallest for pellet appliances due to a lack of or scarcity of organic compounds. Additionally, stable combustion does not exhibit the problem related to the use of different sampling periods. The studied pellet boiler was considered to be state-of-the-art in 2007 and remains on the market today. The PM_1 emissions for nominal output conditions and with reduced primary air input were below the Ecodesign emission limit; however, at low loads, the PM_1 emissions exceeded the limits (Figure 14). As described previously, the use of different pellet raw materials increased PM_1 emissions, whereas the emissions from pellets composed primarily of stem wood remained below the Ecodesign emission limit. Therefore, such emission limits make the use of alternative raw materials highly improbable if flue gas after-treatment techniques are not successfully applied in residential-scale appliances. Because the use of bark also increased NO_X emissions, ESP alone may not be sufficient to reduce emissions according to the regulations; moreover, NO_X reduction techniques should be applied. In addition, ENPlus regulates the use of different raw materials, requiring only stem wood and chemically untreated residues from forest industry to be used in the best pellet class, i.e., ENPlus–A1 (EPC 2013).

In current emission measurement standards, different periods of combustion are sampled from batch combustion appliances; the sampling times in this work were not the same as described in any valid standard. All of the PM emissions from tested batch combustion situations using diluted samples exceeded the Ecodesign emission limits. Moreover, the OC fraction from masonry heaters did not exceed 23%, which is not sufficient to explain the difference based solely on the sampling method. It seems likely that many manufacturers will face problems with the new emission limits, especially for particle emissions. Although the number of tested appliances represents only a few types of appliances, it can be concluded that air staging is a good technique to reduce gaseous emission; however, the particle emissions may not be very significantly from the current technology. Because the lifetime of combustion appliances can be as high as several decades, the new emission limits will not have a quick effect on the total emissions. Therefore, other measures should be introduced in conjunction with the new emission limits to hasten the regeneration of combustion appliances.

The legislation only provides limits for specific PM components in a few special cases, such as in waste incineration, i.e., where fuel can be very heterogenic. Directive 2010/75/EC sets limits for certain heavy metal air pollutions from waste incineration; the limit for the sum of Sb+As+Pb+Cr+Co+Cu+Mn+Ni+V is 0.5 mg/m^3 (11% of O_2, which is equivalent to 0.27 mg/MJ). Such elements are not common in clean woody biomass fuels. Nonetheless, the highest values for pellet combustion were approximately 0.35 mg/m^3 in peat pellet combustion. Moreover, from HFO, the emissions of these metals exceeded the limit (0.45 mg/MJ). Furthermore, inhaled zinc is known to be a harmful metal to human health (Fernandez et al. 2001); however, it is not included in the Directive 2010/75/EC. The highest Zn emissions were from straw pellets, whereas the Zn emissions were higher for pellets containing bark than for commercial pellets.

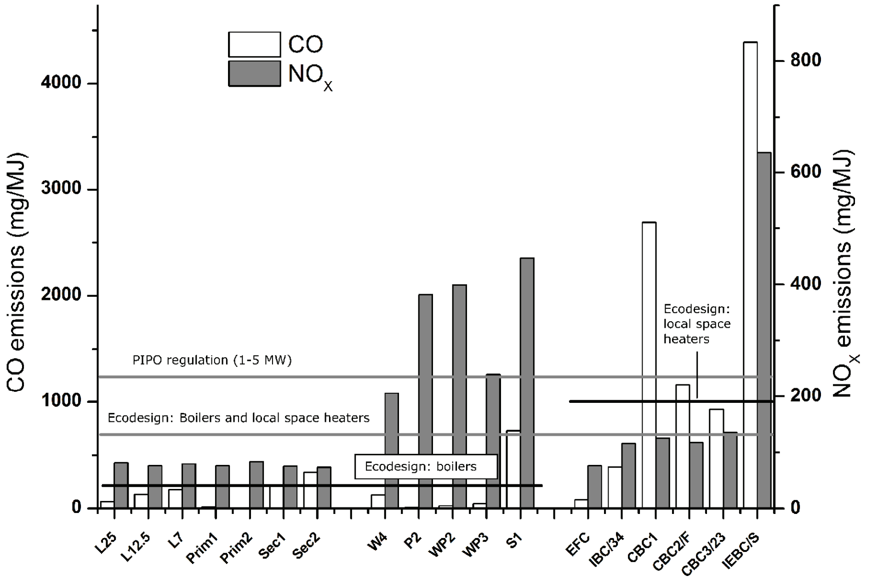


Figure 13. Comparison of gaseous emissions with the different emissions limits. The NOx emission limit in the Ecodesign draft is common for local space heaters and solid fuel boilers.

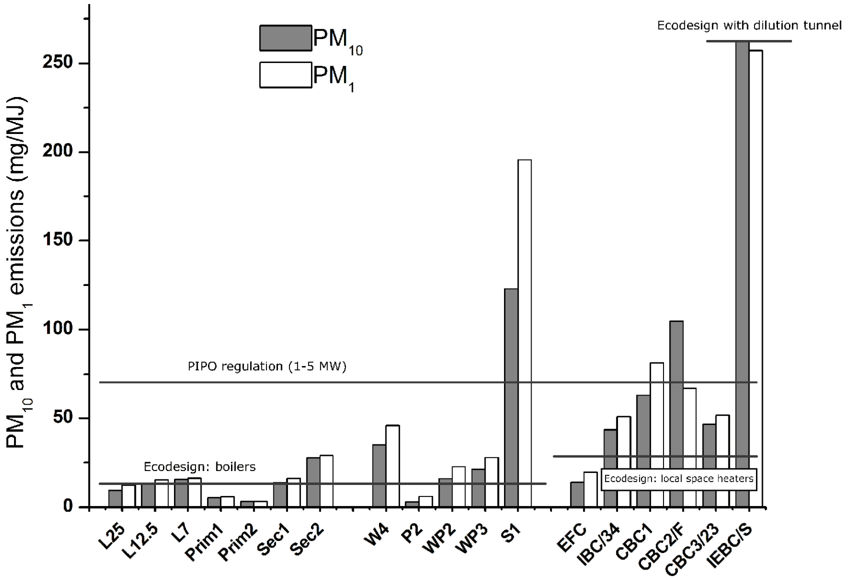


Figure 14. Examples of particle emissions compared with the respective emissions limits. All emission limits are measured in hot flue gas (except with the dilution tunnel), whereas the values presented here are measured in the diluted flue gas.

6 AUTHOR'S CONTRIBUTION

The research presented in this study was primarily performed at the Fine Particle and Aerosol Technology Laboratory at the University of Eastern Finland between 2007 and 2011.

Paper I analyzed pellet boiler emissions for different operational settings. The experiments were performed in a laboratory environment. The experiments were primarily designed by O. Sippula and J. Tissari. The author was primarily responsible for conducting the experiments and writing the manuscript. The data were analyzed and interpreted by the author with the assistance of O. Sippula and J. Tissari and under the supervision of J. Jokiniemi.

Different combustion conditions were tested for several combustion appliances in Paper II; this study was performed under the supervision of J. Jokiniemi and M.-R. Hirvonen. The experimental setup was designed and constructed by the author with the assistance of K. Nuutinen, J. Ruusunen, J. Tissari and O. Sippula. P. Yli-Pirilä and K. Nuutinen were responsible for the PAH analysis, and the metal and ion analyses were conducted by U. Makkonen, K. Teinilä, K. Saarnio and R. Hillamo at the Finnish Meteorological Institute. The data were analyzed by the author and J. Ruusunen, and the author interpreted the results with the assistance of J. Tissari, K. Nuutinen, O. Sippula, J. Ruusunen, P. Jalava, M. Tapanainen, M.-R. Hirvonen and J. Jokiniemi. The author contributed the most to writing the manuscript.

Emissions from pellet fuels made from different raw materials were tested in Paper III using the same experimental setup as in Paper I. This study was performed under the supervision of J. Jokiniemi. The experiments were arranged by O. Sippula and J. Tissari. The author was responsible for the emission measurements, and the data analysis was performed by the author with the assistance of O. Sippula. The results were interpreted by the author with the assistance of the co-authors. The author was the primary writer of the manuscript.

The experiments for Paper IV were conducted at several locations, which included both laboratory and field sites, under the supervision of J. Jokiniemi and M.-R. Hirvonen. The author participated in designing and arranging the experiments and performed the pellet boiler, oil burner and wood-chip-fired power plant experiments with the assistance of T. Kaivosoja and A. Virén. T. Kaivosoja and A. Virén were responsible for the heavy fuel oil emission measurements and the PAH analysis of the samples. T. Torvela and U. Tapper were responsible for the scanning electron microscopy. T. Kaivosoja was primarily responsible for writing the manuscript and analyzing the data. The data were interpreted by all co-authors. The toxicology portion of the study was conducted by P. Jalava, M. Tapanainen and M.-R. Hirvonen.

7 CONCLUSIONS

Residential wood combustion is a significant source of fine particle and gaseous emissions around the globe. The emissions vary depending on the fuel, combustion technology and combustion conditions. User operation often affects combustion behavior in residential-scale appliances. In this thesis, fine particle emissions originating from residential pellet combustion were characterized in different operational situations and using different raw materials as pellet fuel. Moreover, pellet combustion emissions were compared with the emissions from other combustion units used for heat production. These experiments included different combustion situations in batch combustion to represent various combustion appliances, combustion phases and combustion technologies, the combustion of light fuel oil in residential-scale appliances, and the use of wood chips and heavy fuel oil in medium-scale energy production.

Generally, the emissions from automated pellet combustion were low (12.2 mg/MJ with wood pellets); the formed particles primarily contained ash, which originated from the volatile inorganic compounds contained in the fuel; alkali metal compounds were the most important. Pellets can be manufactured from different types of woody raw materials and other biomass. Some of these fuels contain high amounts of alkali metals, which were found to produce high fine particle emissions. The emissions from incomplete combustion were low in pellet combustion; however, these emissions increased for some operation conditions, such as a boiler operating at low loads. The PM_1 emissions from a modern pellet boiler running with bark pellets had the same PM_1 emissions as masonry heaters. Thus, the advantage of using a modern pellet appliance may be partially lost if the wrong fuel type is used.

According to this study, several measures can be used to reduce the PM_1 emissions produced in pellet combustion. First, more precise control of the combustion process, such as advanced staging of combustion air, can be utilized to decrease the release of ash particles from the fuel bed. Reducing primary λ while increasing secondary λ was found to result in lower PM_1 emissions (down to 3.1 mg/MJ). Second, peat as an additive may be used in pellet raw materials to reduce PM_1 emissions. The composition of peat was found to be favorable for inhibiting the release of alkali metals and consequently the formation of fine ash particles. Furthermore, excess PM_1 emissions in residential pellet combustion can be prevented by avoiding the use of fuels that are rich in alkali metals or Cl, e.g., bark or straw.

Both in continuous combustion and in batch combustion, proper combustion technology effectively reduced the emissions of incomplete combustion, such as OC, CO and PAHs. In contrast, it was more difficult to reduce EC emissions. Moreover, when the combustion conditions deteriorated, EC was the first PM component to increase. This phenomenon was highlighted in two separate cases. First, the increased PM_1 emissions for the studied pellet boiler under low load operation was solely due to the elevated EC emissions. Second, there were no clear differences in the EC emissions between conventional and modern masonry heaters even though there was significant effect on the CO, OGC, and PAH emissions. Furthermore, the PAH emissions were more sensitive than other emission components to combustion conditions. Thus, improved combustion technology can affect the harmfulness of the PM via reducing PAH compounds even though the total PM emissions do not decrease.

Optimally operated light fuel oil combustion in a residential-scale burner was not found to be a major source of fine particles (0.1 mg/MJ) due to the efficient combustion process and low amounts of inorganic impurities in the fuel. The PAH emissions from LFO combustion were slightly higher than those of pellet combustion, whereas the PAH emissions from HFO combustion were similar to a modern batch combustion appliance. The emissions from a wood-chip-fired industrial unit were small due to efficient combustion technology and flue gas after-treatment techniques. Such units would also be suitable for alternative biomass fuels because the optimized combustion processes, including flue gas after-treatment techniques, are most likely suitable for high-ash fuels.

This thesis highlights that there are different applications for utilizing biomass fuels for heat production in residential combustion. Current technical solutions provide possibilities for reducing emissions and for using biomass without excess emissions. The emissions from large units are typically well controlled because they are regulated by law. To take full advantage of modern combustion technology in residential-scale appliances, more stringent PM emission limits must be applied. Additionally, because

PM emission limits are set based on their ability to cause adverse health effects, the chemical composition of PM should also be considered. For example, PAH compounds are already monitored in outdoor air; these compounds were shown to reflect the combustion conditions better than particulate mass emissions. A source-based analysis of PAH compounds may provide additional information regarding the potential harmfulness of these emissions.

Continuous combustion appliances, such as pellet boilers and burners, are typically well controlled; however, possibilities remain for reducing the PM emissions under different operating conditions using improved staged combustion. Gasification combustion is an extreme example of staged combustion that has been shown to be beneficial in a small-scale prototype burner. Secondary emission reduction measures, such as electrostatic precipitators, are potentially useful for reducing emissions from residential-scale appliances. These techniques remain under development for residential-scale appliances; their use has not yet been fully demonstrated. ESP technology (or some other secondary reduction technology) should provide emission reductions. First, emissions from existing appliances could be reduced without changing the entire combustion system. Second, high-ash fuels could be used in systems equipped with ESPs without the concern for excess PM emissions. Consumers would be given a choice of either investing in better appliances equipped with an ESP, which comes with the possibility of using low-cost fuels, or purchase a less expensive, yet modern combustion appliance and use first-class fuels. These alternatives would improve the raw material base that is available for pellet production while preventing excess emissions.

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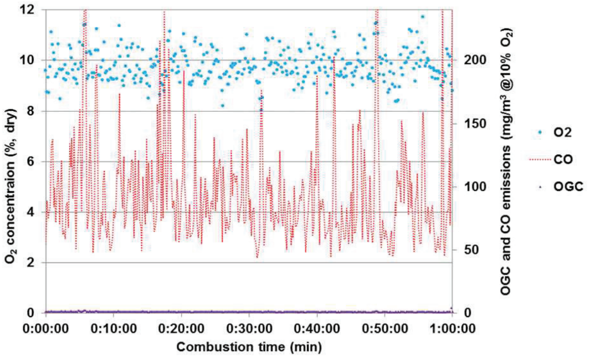
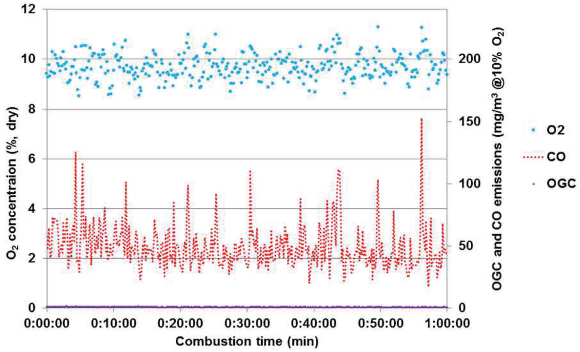
APPENDIX I: TIME SERIES OF GASEOUS COMPONENTS FROM RESIDENTIAL COMBUSTION

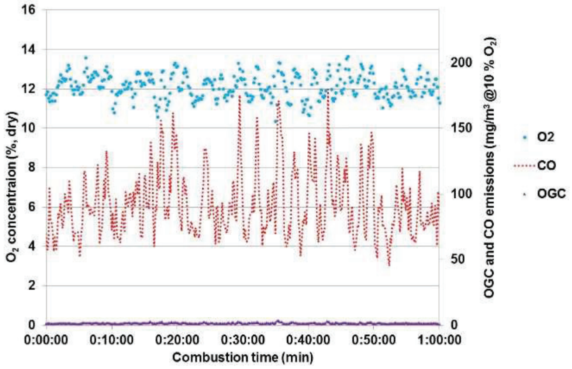
Figure 1: O_2, CO and OGC concentrations as a function of time in the different experimental cases.



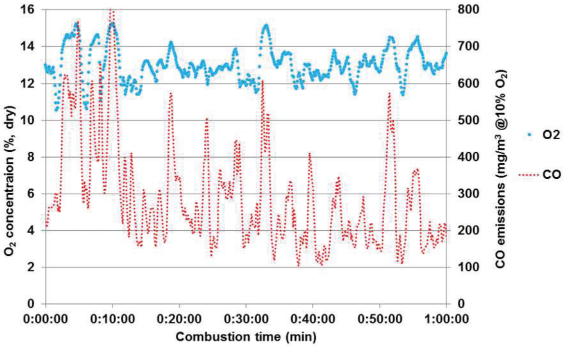
Pellet combustion: peat (20%) and pine bark (80%).



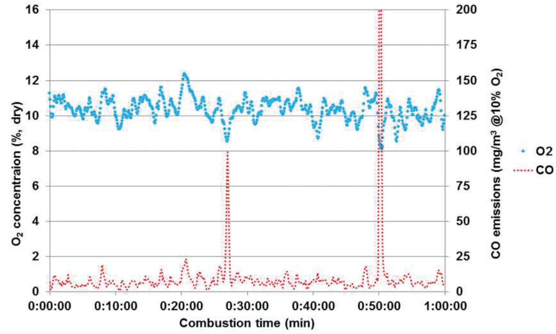
Pellet combustion: peat (40%) and pine bark (60%).



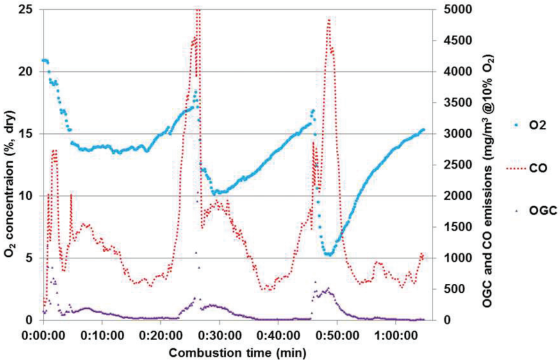
Pellet combustion: nominal load (L_{25}).



Pellet combustion: low load (L$_{12.5}$).



Pellet combustion: reduced primary air (Prim$_2$).



Conventional masonry heater (CBC3).

Paper I

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ARTICLE

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Effects of Air Staging and Load on Fine-Particle and Gaseous Emissions from a Small-Scale Pellet Boiler

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S *Supporting Information*

ABSTRACT: Fine-particle and gaseous emissions from a modern small-scale pellet boiler were studied with different air-staging settings and under different load operations. Commercial wood pellets were used in the boiler, which worked with a top-feed fuel input. Partial load operation experiments included half-load 12.5 kW and low-load 7 kW. In air-staging experiments, the amounts of primary air were decreased by 71 and 82% while simultaneously keeping constant total air/fuel ratios. This was found to result in considerably lower emissions than during normal full-load operation with factory settings. The reduction in fine-particle emissions was based on both a decrease in alkali metal emissions and emissions of unburnt carbonaceous particles. However, when the amounts of secondary air were decreased by 17 and 33%, there were higher emissions of both fine particles and gases during full-load operation, especially of emission components originating from incomplete combustion. The primary air/secondary air ratio correlated with CO, PM_1, K, EC, and SO_4 emissions. Furthermore, correlations were found between the primary air/fuel ratio and particle geometric mean diameter (GMD) and between the secondary air supply and GMD. These correlations were seen with all measured points, which indicates that they apply to all of the operational situations that were studied. The results show that there is significant potential for decreasing particle emissions from automated pellet combustion systems by optimizing combustion air staging in the furnace.

1. INTRODUCTION

Wood-based biomass fuels are used for heat and energy production because they reduce carbon dioxide (CO_2) emissions and fossil fuel consumption. The European Union has set targets to increase the overall use of biomass to control CO_2 emissions.[1] To achieve these goals, one way to use wood fuels is in small-scale combustion in households. However, combustion of wood fuels, especially in small-scale heat production, is known to cause major emissions of pollutants, such as organic gaseous carbon (OGC), particulate matter (PM), and polycyclic aromatic hydrocarbons (PAHs) because of poor combustion control and lack of flue gas after treatments.[2−4] Furthermore, burning biomass generally produces higher amounts of such emissions than oil, which is the fuel often replaced by biomass in small-scale use.[5] Fine particles (PM_1, fine particles with aerodynamic diameter under 1 μm) are known to have adverse effects on human health,[6] and increases in biomass combustion can lead to increased concentrations of PM in the atmosphere. In addition, fine particles may have negative effects on combustion appliances. Furthermore, emissions of wood combustion are important precursors of secondary organic aerosol.[7]

Automation of small-scale combustion appliances has been shown to provide good control of the combustion process similar to large-scale combustion and to accomplish better efficiency and lower emissions.[4] Wood pellets are well-suited to automatic heating appliances and have the potential to grow in household energy markets. Pellet appliances equipped for continuous combustion can easily achieve good combustion efficiency because of stable fuel quality[8] and combustion process. Even though the gaseous and PM_1 emissions from pellet combustion are generally low compared to the emissions from log-fueled batch combustion appliances,[4,5] increased emissions may occur during some operational procedures, such as cleaning periods[9] and periods of lower load,[5,10−12] which are common during normal operation. Secondary emission reduction measures are not yet common in small-scale combustion devices even though there are a number of devices being developed with varying flue gas after-treatment techniques. Primary reduction of emissions, such as by optimized air staging, is a strategy for reducing emissions that is likely to be favored by boiler manufacturers because it enhances the completeness of combustion, thus increasing appliance efficiency while being more feasible than after-treatment techniques that require extra investments, maintenance, materials, and space.

Particle emissions from small-scale combustion usually contain mostly PM_1.[9,13] PM_1 emissions from pellet combustion are generally low and are mainly formed of alkali salts. Emissions associated with incomplete combustion, such as elemental carbon and organic carbon, are low.[9,14] This is a result of the design and combustion control in pellet appliances. Ash particles are mainly formed from alkali compounds that vaporize in the hot temperatures of the flame or fuel bed. Cooling of the flue

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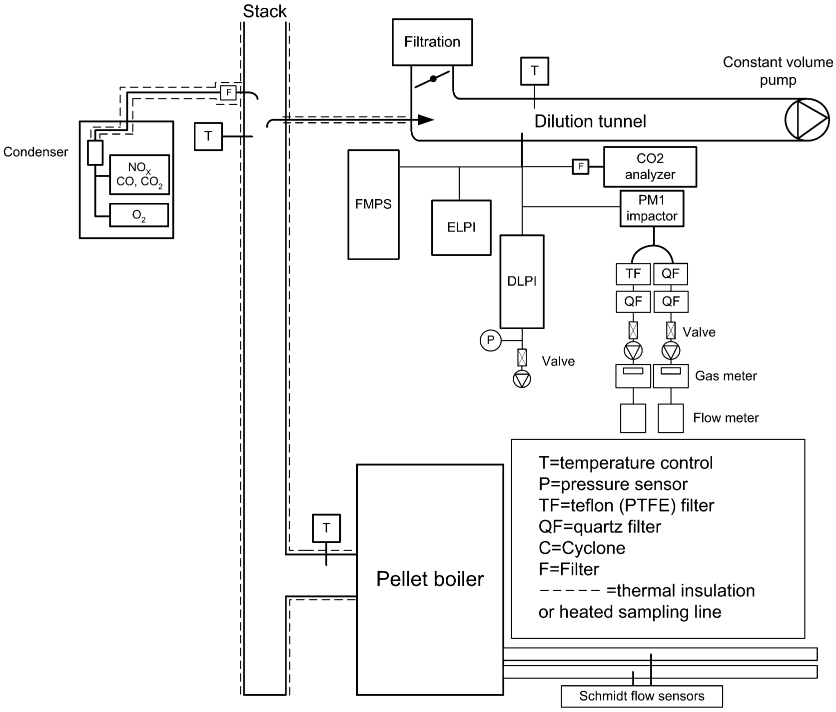

Figure 1. Schematic drawing of the experimental setup.

gases or chemical reactions cause the vaporized components to saturate and condense, forming fine particles.[9,15]

The formation of emissions can be affected by staging of the combustion air supply in the furnace.[16] The air supply in grate-fired appliances is divided between primary air supplied through the grate and secondary air supplied later above the grate. It has been reported that, in staged biomass combustion, the primary combustion should be understoichiometric, with a sufficient residence time (about 0.5 s) between primary and secondary combustion zones.[8] Air staging has been used in large-scale energy production for reduction of nitrogen oxide (NO_x) emissions.[17,18] Air staging has also been used at small scales, especially to decrease the emissions of incomplete combustion. It has been reported that reducing primary air flow through the fuel bed results in lower evaporation of alkali metals. This is due to either lower fuel bed temperatures[16] or reducing conditions in the fuel bed, which convert K oxides into K salts that have significantly higher volatilization temperatures and are thus converted into the grate ash.[8] However, too large of air flow through the fuel bed has been found to decrease the residence time in the primary combustion zone and to increase particle emissions.[19] Furthermore, no correlations were found between particle concentrations in the primary combustion zone and in the flue gas, which shows that the oxidation in the secondary combustion zone has a major effect on emission factors.[19] Previous studies show that there are ways to further develop the combustion process to decrease the emissions in normal combustion situations in small-scale pellet combustion.

In the present study, the aim was to investigate the effects of partial load and air staging on particle and gaseous emissions from a modern small-scale pellet boiler. The goal was also to investigate if combustion parameters, such as combustion air supply, air distribution, and air/fuel ratios, could be linked with emission characteristics, such as PM_1 and particle number emissions, particle size, and particle chemical composition.

2. EXPERIMENTAL SECTION

Combustion experiments were performed in a laboratory environment with a 25 kW pellet boiler suitable for household heat production. Heat from the pellet boiler system was transported to a 200 kW heat exchanger to cool the system and enable stable operation. The flue gases were led to an approximately 3 m high insulated steel stack (Figure 1). After the stack, a hood equipped with a flue gas fan was used to transport the flue gases outside. There was a space between the stack and the hood to ensure natural draft in the stack and in the appliance. A portion of the flue gases were transported to a dilution tunnel through an insulated and heated sample line. The diameter of the sample line was 12 mm, and it was heated to 140 °C to prevent cooling and condensation in the line. The dilution tunnel was built according to the International Organization for Standardization (ISO) standard,[20] and it has been described in studies on different kinds of emission measurements from biomass combustion.[9,13,21] The air used to dilute flue gases in the tunnel was taken from the laboratory room air and was filtered in three stages: a prefilter removed coarse particles; a chemical filter removed hydrocarbons and nitrogen oxides; and a post-filter removed fine particles. The sample flow from the stack to the dilution tunnel was drawn by adjusting a vacuum in the dilution tunnel. To control the process and the setup during the experiment, temperatures were measured continuously at three different locations: after the pellet boiler at the entrance into the

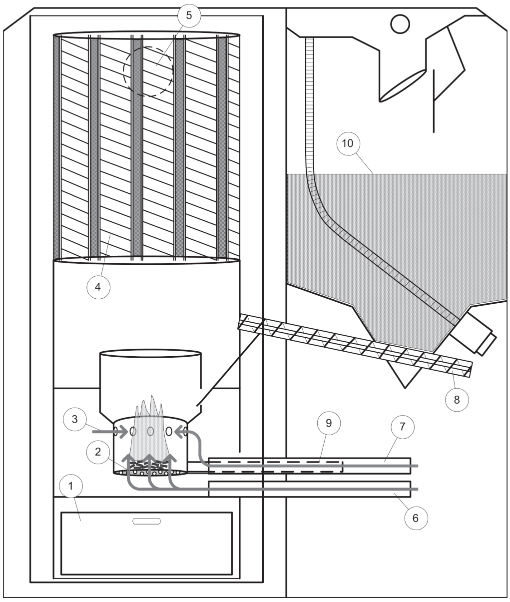

Figure 2. Sketch of the pellet boiler used in this study: 1, ash box; 2, grate and primary air supply; 3, secondary air supply; 4, heat exchanger; 5, flue gas outlet; 6, primary air inlet; 7, secondary air inlet; 8, pellet feeding screw; 9, ignition fan; and 10, pellet storage.

stack ($T_{\text{flue 1}}$), in the stack at the point that samples were drawn into the dilution tunnel ($T_{\text{flue 2}}$), and in the dilution tunnel (T_{sample}) (Figure 1).

2.1. Combustion Appliance and Operational Practices.

The combustion appliance used in these experiments was a pellet boiler with a 25 kW maximum load (Biotech Energietechnik GmbH, model PZ-RL). The pellet boiler operates with a top-feed fuel input and includes an integrated burner and boiler (Figure 2). The boiler can be operated continuously between the loads of 6 and 25 kW. It is equipped with logic-controlled fans for the supply of combustion air. The primary air was fed in through holes in the grate at the bottom of the cylindrical furnace. The width of the grate was approximately 110 mm, and the diameter of each hole was approximately 7 mm. Secondary air was fed in 100 mm above the grate through 12 holes with a diameter of 15 mm each. The furnace widened approximately 130 mm above the grate. Commercial wood pellets originating from Finland were used in the study. The primary pellet raw material was pine stem wood, and details of the fuel composition is presented in Table 1.

Combustion experiments were performed with three different operational manipulations: partial loads, reduced primary combustion air supplies, and reduced secondary combustion air supplies. Normal operation was assumed to obtain nominal load of 25 kW (L_{25}), represented as a baseline, to which the other settings were compared. Partial loads included half load, about 12.5 kW ($L_{12.5}$), and low load, about 7 kW (L_7). Low load was selected as a partial-load condition where the boiler still operates continuously. Partial loads were created by adjusting the load in the boiler.

Primary air settings were selected from the settings of the pellet boiler, where the normal average air flow of 176 liters per minute (lpm) was reduced to 75% (Prim_1) and 50% (Prim_2). Secondary air settings were also selected from the boiler setting, where the average secondary air flow of 302 lpm was reduced to 75% (Sec_1) and 50% (Sec_2). However, it was found that these setting values in the boiler did not fully correlate with the real measured combustion air flows. In the cases of Prim_1 and Prim_2, the primary combustion air flows decreased by 71 and 82%, to averages of 50 and 15 lpm, respectively, and in the cases of Sec_1 and Sec_2, the secondary combustion air flows decreased by 17 and 33% to 250 and 202 lpm, respectively. Combustion air flows are presented in more detail in Table 2. Reductions of primary and secondary air flows were found to decrease load because of lower fuel supply. This occurred because, in normal use, the combustion process in this pellet boiler is controlled by adjusting the air flows and the fuel supply. The estimated loads are presented in Table 3.

Table 1. Properties of the Fuel Used

moisture (%)	7.5
ash content (%, 550 °C)	0.2
net calorific value (MJ/kg)	18.91
ash fusibility, deformation (°C)	1450
bulk density (g/L)	633
S (m %)	<0.02
C (m %)	51.2
H (m %)	6.4
N (m %)	<0.1
Cl (m %)	0.007
Si (mg/kg)	140
K (mg/kg)	420
Na (mg/kg)	<20
Zn (mg/kg)	7.04
Ca (mg/kg)	633
Fe (mg/kg)	52.6

Combustion air supplies were measured before they entered the pellet boiler with Schmidt (model SS 20.60) flow sensors that were installed in flow tubes upstream of the combustion air fans. The large diameters of the flow tubes (diameter of 101.7 mm and primary air tube of 44.5 mm in Prim_1 and Prim_2) ensured that only a negligible pressure loss was caused by the measurement. Thus, the flow measurement did not affect the combustion process.

Each of the combustion experiments were performed in a preheated pellet boiler. The boiler was turned on 3 h before the start of the experiment, and the warming was performed on full load. Each variable parameter for the upcoming experiment was changed 1 h before the start of the experiment, which was found to be sufficient for the combustion process to stabilize. The boiler worked automatically during each experimental period (3−4 h), and the user had no control over the combustion process.

2.2. Gas Measurements.

Gas measurements were made in the undiluted flue gas in the stack. A combination of gas analyzers (ABB Cemas gas-analyzing rack) continuously measured CO_2, carbon monoxide (CO), oxygen (O_2), and NO_x concentrations. NO_x results were calculated and are further presented as NO_2 equivalents. The CO_2 concentration was also measured in the dilution tunnel with a CO_2 analyzer (ABB AO2040, Uras 14) to continuously calculate and control the dilution ratio (DR).[3]

2.3. Particle Measurements and Analyses.

Particle measurements were made in the dilution tunnel. DR varied between 101 and 124, except in Sec_2, where DR needed to be increased (DR 1220) to prevent the online particle measurement devices from exceeding the measurement range. The variation in DRs was small within each experimental period (Table 2). Particle concentrations were corrected by multiplying the results by the DR. All of the emission results were calculated in relation to the fuel energy input to the burning process.[22]

Particle number size distributions were measured with an electrical low-pressure impactor (ELPI, Dekati Ltd.) and a fast mobility particle

Table 2. Flue Gas Temperatures, Dilution Ratios, and Combustion Air Flows[a]

	L_{25}	$L_{12.5}$	L_7	$Prim_1$	$Prim_2$	Sec_1	Sec_2
$T_{flue\ 1}$ (°C)	154 ± 1.4	84 ± 1.5	75 ± 0.6	127 ± 1.0	110 ± 1.1	139 ± 2.0	117 ± 0.7
$T_{flue\ 2}$ (°C)	99 ± 1.0	51 ± 0.7	46 ± 0.3	79 ± 0.8	69 ± 0.6	89 ± 1.5	74 ± 0.4
T_{sample} (°C)	30 ± 0.7	29 ± 0.8	30 ± 0.1	29 ± 0.4	31 ± 0.3	30 ± 1.0	28 ± 0.3
dilution ratio	124 ± 6	103 ± 7	102 ± 7	119 ± 3	118 ± 5	120 ± 5	1220 ± 84
primary air flow (lpm)	176 ± 9	84 ± 9	49 ± 23	50 ± 7	15 ± 9	183 ± 7	183 ± 7
secondary air flow (lpm)	302 ± 15	129 ± 15	90 ± 11	320 ± 29	315 ± 21	250 ± 12	202 ± 7
total air flow (lpm)	478	214	139	371	331	434	385

[a] $T_{flue\ 1}$ was measured in the flue gas where the flue gases entered the stack. $T_{flue\ 2}$ was measured at the point where the sample was taken to the dilution tunnel. T_{Sample} was measured at the point where the sample was taken from the dilution tunnel. The values from continuous measurements are average values with standard deviations.

Table 3. Gaseous and Particle Emission Factors and Fine-Particle Characteristics[a]

	L_{25}	$L_{12.5}$	L_7	$Prim_1$	$Prim_2$	Sec_1	Sec_2
CO	63 ± 56	132 ± 113	178 ± 102	13.6 ± 11	3.55 ± 7.06	213 ± 189	335 ± 292
NO_x	81 ± 3.8	76 ± 6.4	79 ± 6.8	76 ± 2.4	83 ± 3.4	75 ± 2.8	73 ± 2.9
O_2 (%)	9.8 ± 0.8	13.3 ± 1.0	14.7 ± 0.8	10.1 ± 0.5	10.4 ± 0.6	9.5 ± 0.7	10.1 ± 0.9
λ_{Tot}	1.93 ± 0.30	2.69 ± 0.34	3.41 ± 0.44	1.95 ± 0.09	1.99 ± 0.12	1.84 ± 0.12	1.95 ± 0.17
λ_{Prim}	0.71	1.06	1.20	0.27	0.09	0.78	0.93
λ_{Sec}	1.22	1.63	2.21	1.68	1.90	1.06	1.02
$\lambda_{Prim}/\lambda_{Sec}$	0.58	0.65	0.54	0.16	0.05	0.73	0.91
load[b]	25	11.2	7.3	19.4	17.3	22.7	20.1
PM_1	12.2 ± 1.0	15.3 ± 1.1	16.3 ± 0.9	5.9 ± 0.4	3.0 ± 0.7	16.1 ± 1.2	29.0 ± 1.8
OC	0.28 ± 0.46	1.37 ± 1.75	0.46 ± 0.52	0.53 ± 0.26	0.09 ± 0.14	1.35 ± 1.34	3.06 ± 1.85
EC	0.75 ± 0.21	7.84 ± 0.26	8.27 ± 0.53	0.55 ± 1.78	0.00 ± 0.01	4.97 ± 0.47	14.0 ± 1.60
CO_3	0.42 ± 0.51	0.75 ± 0.65	0.57 ± 0.52	0.38 ± 0.66	0.26 ± 0.44	1.22 ± 0.41	5.64 ± 5.60
Ca	0.33	0.27	0.37	0.28	0.42	0.32	2.87
K	2.76	2.34	2.19	1.83	1.27	3.22	5.24
Na	0.11	0.13	0.13	0.13	0.15	0.19	0.86
Zn	0.14	0.16	0.16	0.14	0.15	0.13	0.25
Fe	0.22	0.19	0.31	0.23	0.19	0.13	0.12
SO_4	2.22	1.88	1.88	1.56	0.65	1.99	2.21
others analyzed	0.72	0.23	0.28	0.21	0.29	0.20	1.28
release fraction from fuel to PM_1							
K (%)	12.4	10.5	9.9	8.2	5.7	14.5	23.6
Zn (%)	38.3	42.4	43.4	38.3	40.3	35.0	67.7
number emissions, ELPI	$1.56 \times 10^{13} \pm 3.01 \times 10^{12}$	$1.38 \times 10^{13} \pm 7.96 \times 10^{12}$	$1.20 \times 10^{13} \pm 4.47 \times 10^{12}$	$2.22 \times 10^{13} \pm 2.53 \times 10^{12}$	$1.23 \times 10^{13} \pm 2.11 \times 10^{12}$	$2.88 \times 10^{13} \pm 1.44 \times 10^{13}$	$3.82 \times 10^{13} \pm 2.23 \times 10^{13}$
FMPS[c]	$3.01 \times 10^{13} \pm 3.08 \times 10^{12}$			$2.05 \times 10^{13} \pm 1.81 \times 10^{12}$	$1.53 \times 10^{13} \pm 1.56 \times 10^{12}$	$2.94 \times 10^{13} \pm 4.94 \times 10^{12}$	
GMD, ELPI (FMPS[c])	68.5 (46.6)	79.6	82.6	58.7 (49.8)	53.7 (41.3)	70.7 (61.9)	77.9
MMD, DLPI	124	181	336	101	136	132	158

[a] CO, NO_x, PM_1, EC, OC, CO_3, Ca, K, Na, Zn, Fe, SO_4, others analyzed, in units of mg MJ^{-1}; number emissions, in units of number MJ^{-1}; and GMD and MMD, in units of nm. The chemical composition was analyzed from one filter sample only, whereas the other compositions (OC/EC and mass) were analyzed from three samples. The values from continuous measurements are average values with standard deviations. Other analyzed chemical species have been presented in more detail in the Supporting Information. [b] Load is an estimation, except L_{25}. It is calculated from nominal load and total combustion air flows. [c] Because of some operational problems with FMPS, the results are only presented for N_{25}, $Prim_1$, $Prim_2$, and Sec_1.

sizer spectrometer (FMPS, model 3091, TSI, Inc.). The ELPI was operated with a flow rate of 10 lpm and cutoff diameters from 24 nm to 9.38 μm with sintered impaction plates. FMPS uses a flow rate of 10 lpm and measures particles in the range from 5.6 to 560 nm. Particle mass size distributions were measured with a 13-stage Dekati low-pressure impactor (DLPI, Dekati Ltd.) with a flow rate of 10 lpm and cutoff diameters from 28 nm to 9.84 μm. Aluminum foils, greased with a mixture of toluene and Apiezon-L vacuum grease (M and I Materials Ltd.), were used on the impactor stages in the DLPI. Two parallel filter collections were made. For the first filter collection system, a polytetrafluoroethylene (PTFE) filter (Pall Corporation, P/N R2PJO47) was placed on a stainless-steel filter holder (Gelman Sciences 2220) and particles larger than 1 μm were removed with a pre-cutoff impactor (Dekati Ltd.). For the second filter collection system, identical pre-cutoff impactor and filter holders were used with a set of three quartz filters (Pallflex, Tissuequartz) and one PTFE filter (see Figure 1). Elemental carbon (EC), organic carbon (OC), and carbonate carbon (CO_3) were analyzed from the quartz filter samples with a thermal−optical method[23] using an OCEC carbon aerosol analyzer from Sun Laboratories, Inc. (model 4 L). The analyses were performed according to the National Institute for Occupational Health procedure.[24] A detailed description of the method has been presented elsewhere.[9,25] All of the filters and impactor foils were weighed before and after the collection at a stable room temperature of 20 °C and a relative humidity of 40%. Filters were kept in the weighing room for at least 24 h before weighing for them to stabilize. Weighing was performed with a microbalance with 1 μg sensitivity (Mettler Toledo, MT5) and a charge eliminator (Staticmaster, Po-210). The elemental analyses (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Th, Ti, Tl, U, V, and Zn) were performed by inductively coupled mass spectrometry (ICP−MS; hydrofluoric acid and nitric acid dissolution). Anions (Br, Cl, F, SO_4, and NO_3) were analyzed by ion chromatography (IC; water dissolution).

3. RESULTS

Flue gas temperatures that were measured after the flue gas entered the stack ($T_{\text{flue 1}}$) varied between 75 °C (L_7) and 154 °C (L_{25}) (Table 2). The variation within each experiment was small, which indicates that the combustion process was stable during the experiments. No significant changes in the diluted sample temperatures (T_{sample}) measured in the dilution tunnel were observed, with temperatures varying by just 3 °C between the different experiments.

The highest O_2 concentrations were seen with partial loads (Table 3), while the reduction of primary and secondary air did not have any major effect on flue gas O_2 concentrations. Total air/fuel ratios (λ_{Tot}) were calculated from O_2 concentrations according to Finnish Standards Association (SFS) standard 5624.[22] In addition, air/fuel ratios were calculated for primary and secondary combustion zones (λ_{Prim} and λ_{Sec}) based on the measured primary and secondary air flows and λ_{Tot}. λ_{Prim} is defined as the air/fuel ratio calculated on the basis of the combustion air supply through the grate, while λ_{Sec} is the air/fuel ratio calculated on the basis of the air supplied through the secondary nozzles above the grate. The lowest λ_{Tot} was measured from Sec_1 (1.88), and the highest λ_{Tot} was measured from L_7 (3.41). λ_{Prim} varied between 0.09 (Prim_2) and 1.20 (L_7), and λ_{Sec} varied between 1.02 (Sec_2) and 2.21 (L_7) (Table 3).

Combustion air flows were measured continuously in each experiment. Primary combustion air supply varied between 15 lpm (Prim_2) and 183 lpm (Sec_1 and Sec_2) (Table 2). Secondary combustion air supply varied between 90 lpm (L_7) and 320 lpm (Prim_1). The results in Table 2 show that, when the primary air supply was reduced, the secondary air supply automatically increased slightly (13−18 lpm). The reverse was also true with reduction in the secondary air supply, leading to an increase in the primary air supply of about 7 lpm.

3.1. Gaseous Emissions. The emissions of gaseous compounds, CO and NO_x, are presented in Table 3. The CO emissions were clearly affected by the different operational changes between each experiment. On full load (L_{25}), the CO emission was 64 mg/MJ, and by comparison, it increased 2-fold on half load ($L_{12.5}$) and 2.7-fold on low load (L_7). The CO emissions from Prim_1 and Prim_2 were only 21 and 5.6% that of L_{25}, respectively. The reduction of secondary air increased CO emissions 3.4- and 5.3-fold in Sec_1 and Sec_2, respectively. CO emissions also varied significantly within each experiment. No clear variation in NO_x emissions between the different experiments was observed (Table 3). The highest NO_x emissions were measured in Prim_2 (83 mg/MJ), and the lowest NO_x emissions were measured in Sec_1 (73 mg/MJ).

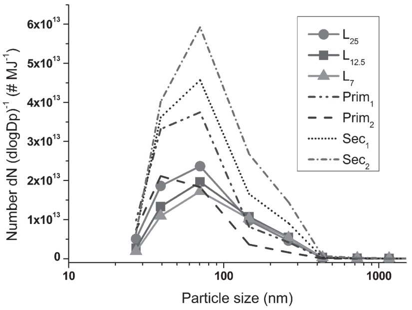

Figure 3. Number-size distributions, measured with ELPI.

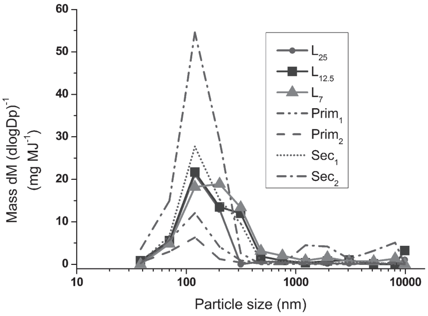

Figure 4. Mass size distributions, measured with DLPI.

3.2. Particle Number Emissions and Number Size Distribution. The particle number emissions measured with ELPI varied between 1.20 × 10^{13} number MJ^{-1} from L_7 and 3.82 × 10^{13} number MJ^{-1} from Sec_2 (Table 3). The variations in particle number emissions were generally low within each experimental period, but it was clear that the variations in number emissions increased when the amount of secondary air was reduced in Sec_1 and Sec_2. In comparison to particle number emissions by L_{25}, there was slight decreases in $L_{12.5}$, L_7, and Prim_2 and clear increases in Prim_1, Sec_1, and Sec_2.

The particle geometric mean diameters (GMDs) presented in Table 3 increased when partial loads were used ($L_{12.5}$ and L_7) or secondary air supply was reduced (Sec_1 and Sec_2). However, GMD decreased when primary air supply was reduced (Prim_1 and Prim_2). The smallest GMD was measured from Prim_2 (53.7 nm), and the largest GMD was measured from L_7 (82.6 nm). The L_{25} GMD was 68.5 nm. Unimodal number distributions were seen in all experiments. Because of the low accuracy of ELPI for measuring small particles, the differences in particle sizes are not clearly visible (Figure 3). However, Prim_2 clearly has the smallest GMD, and the differences in number emissions can be clearly observed.

3.3. Particle Mass Emissions and Mass Size Distribution. PM_1 emission was 12.2 mg/MJ at L_{25} (Table 3). In comparison to L_{25}, PM_1 emissions increased slightly when partial loads

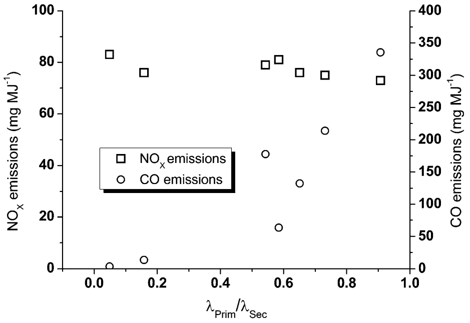

Figure 5. NO$_x$ and CO emissions as a function of $\lambda_{Pri}/\lambda_{Sec}$.

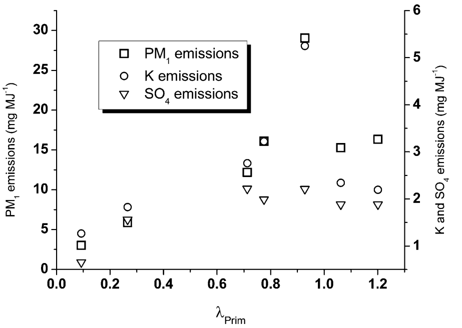

Figure 7. PM$_1$, K, and SO$_4$ emissions as a function of λ_{Pri}.

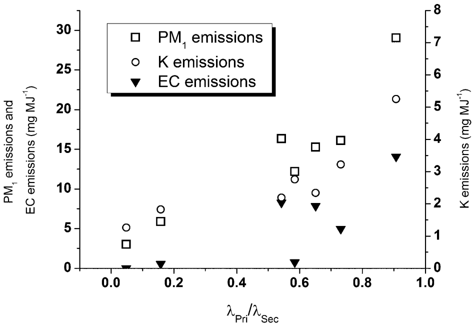

Figure 6. PM$_1$, EC, and K emissions as a function of $\lambda_{Pri}/\lambda_{Sec}$.

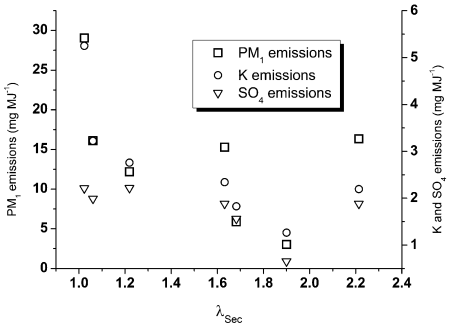

Figure 8. PM$_1$, K, and SO$_4$ emissions as a function of λ_{Sec}.

(15.3 mg/MJ from $L_{12.5}$ and 16.3 mg/MJ from L_7) were used and when secondary air supply was reduced (16.1 mg/MJ from Sec_1 and 29.0 mg/MJ from Sec_2). Similar to CO emissions, PM_1 emissions decreased when the primary air supply (5.9 mg/MJ from $Prim_1$ and 3.0 mg/MJ from $Prim_2$) was reduced.

Mass mean diameters (MMDs) were calculated from the DLPI results (Table 3). The smallest MMD was measured from $Prim_2$ (101 nm), and the largest MMD was measured from L_7 (336 nm). The differences in mass size distributions between each experiment are clearly distinguishable in Figure 4. Figure 4 also shows a possible second mode in Sec_2.

3.4. Particle Chemical Composition. The chemical compositions of the particle samples in all of the experiments were mainly composed of EC, K, and SO_4 (Table 3). A higher amount of OC was only detected from Sec_2. The emissions of EC increased significantly when partial loads were used in comparison to the emission factors from the full load (Table 3). The increase in EC emissions from L_{25} to $L_{12.5}$ and L_7 was 10.4- and 11-fold, respectively. The reduction of the secondary air supply also affected the EC emissions with 6.6- and 18.6-fold increases above L_{25} from Sec_1 and Sec_2, respectively. Reduction of the primary air supply decreased the EC emissions of $Prim_1$ to a level 30% below that of L_{25}. In $Prim_2$, the EC emissions were practically nonexistent (under the detection limit).

The variations in OC emissions were much smaller than those of EC. However, a similar trend can also be seen for OC; partial loads and reduced secondary air supply increased the OC emissions, but reduced primary air supply decreased the OC emissions.

The proportions of K and Zn in fuel that were released as fine particles, calculated on the basis of the fuel chemical composition, varied between 5.7−24 and 35−68%, respectively (Table 3). The K release as fine particles decreased for $Prim_1$ and $Prim_2$ and increased for Sec_1 and Sec_2. In comparison to L_{25}, the K released from partial loads was slightly decreased. The Zn release as fine particles varied less and was only clearly different for Sec_2.

3.5. Correlations between Operational Settings and Emissions. Connections between operational settings and emission characteristics were checked by linear correlations. Correlations between operational settings, such as primary air flow, secondary air flow, total air/fuel ratio, primary air/fuel ratio, and secondary air/fuel ratio, and characteristics of gaseous and particle emissions were tested. Selected correlations are presented in Figures 5−9. It was found that some settings and emissions correlated with all 7 data points, while others correlated with only 5 data points when the partial load experiments were excluded from the tests. However, the test was performed with 5 data points too because the combustion conditions in partial load experiments differed significantly from the other experiments, for example, by a higher air/fuel ratio. Some factors, such as OC and EC were also found to correlate linearly with primary air flow and secondary air flow but with only 3 data points (for example, in L_{25}, $Prim_1$, and $Prim_2$). These correlations may be realistic, but with such a limited number of data points, they will not be further discussed.

The primary air/fuel ratio, λ_{Prim}, was found to correlate linearly with GMD (7 measurement points) (Figure 7) and with

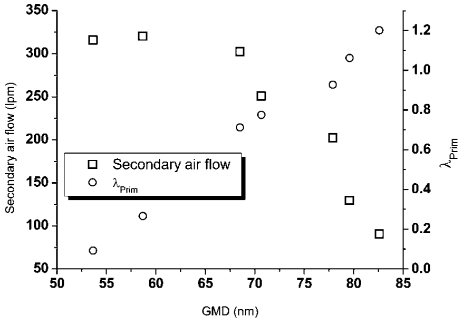

Figure 9. Secondary air flows and λ_{Pri} as a function of GMD.

K and SO_4 emissions and the release of K as fine particles (5 measurement points, with partial load results excluded). The reduction of secondary air/fuel ratio, λ_{Sec}, seemed to increase K and SO_4 emissions and the release of K and Zn as fine particles when partial load experiments were excluded from the test (5 measurement points; Figure 8). The secondary combustion air flows correlated linearly with GMD (7 measurement points), K emissions and the release of K to fine particles (5 measurements points, with partial load results excluded). The $\lambda_{\text{Prim}}/\lambda_{\text{Sec}}$ ratio was found to correlate linearly with CO, PM_1, K, EC, and SO_4 emissions (7 measurement points) (Figures 5 and 6).

4. DISCUSSION

The benefits of the new automated boilers over the old type of boilers are that the load can be adjusted flexibly according to the heat requirement and, thus, there is less need to shut down and start up, which has lowered emissions, together with improved combustion technology. In this study, emission factors for all experimental settings were low compared to the old type of pellet boiler/burners and batch combustion appliances, such as masonry heaters and stoves,[4,5,21] and at a similar level to modern pellet boilers.[4,10,12]

4.1. Effect of Partial Load. It has previously been reported that the emissions from a pellet boiler increase with continuous combustion at partial loads.[5,10] In this study, PM_1 emission factors increased slightly but the CO and EC emission factors increased more significantly. Air/fuel ratios were significantly higher at partial-load conditions than at full-load conditions. The air distribution also changed; a larger amount of air was inserted as primary air with partial loads. A change in air distribution can affect mixing in the primary and secondary combustion zones or change the residence time and temperatures inside the furnace. A lower temperature because of a higher air/fuel ratio can decrease the oxidation rate of CO,[26] and a higher air/fuel ratio and air supply through the fuel bed has been reported to increase the emissions from pellet combustion.[16] It is also possible that the secondary air, which is inserted through 12 15 mm diameter holes, lost its capability to penetrate the furnace when the secondary air supply decreased, because it is known that the penetration capability weakens when the air is distributed to the furnace walls through too many inlets around the furnace.[27]

4.2. Effect of Primary Air Reduction. The amount of primary air is known to affect the temperature in the fuel bed and the release of ash particles; the reduction of primary air has been found to decrease the temperature in the primary combustion zone and lead to reduced volatilization of alkali metals in the fuel bed,[8,16] whereas too large of air flow through the fuel bed has been found to increase the temperature in the fuel bed and to increase fine-particle emissions.[16] Furthermore, primary air affects the composition of the product gas formed in the primary combustion zone. This also affects the combustion behavior in the secondary combustion zone. If the energy content of the product gas from primary combustion is too low, the secondary combustion may not be efficient enough.

Reduction of the primary air supply generally had a positive effect on emission factors; emissions of PM_1 and CO decreased significantly (Table 3), as well as the emissions of K and SO_4 and the release of K as fine particles (Figure 7). The release behavior of K and other inorganic species may be affected by several factors. First, a very low primary air supply is likely to create a local environment similar to a gasification combustion process, where the fuel is first gasified and the combustion of the gasified fuel occurs mainly in the secondary combustion zone, which is likely to result in lower fuel bed temperatures.[25] Second, a decrease in primary air produces more reducing conditions, which may also affect the release behavior of inorganic elements. In addition, a low primary air supply and consequent high secondary air supply increases secondary air jet velocities, which enhances mixing in the secondary combustion zone and can be seen in very small emissions of unburnt gases and particles in Prim_1 and Prim_2.

λ_{Prim} was 0.71 in L_{25} and dropped to 0.27 (Prim_1) and 0.09 (Prim_2) (Table 3). Because the λ_{Prim} was very low for Prim_1 and Prim_2 (0.09, equaling 4.5% of the total air flow), it is very likely that some secondary air also acted as primary air because of the possible back-mixing of secondary jets downward in the combustion chamber. In addition, the primary air factors were much lower than what is suggested to be an optimal primary air/fuel ratio from the point of view of efficiency and emissions.[28] It must be pointed out that, in this appliance, with a top-feed fuel input, a false air through the fuel input channel would end up in the secondary combustion zone rather than in the primary combustion zone. We could not continuously measure the load of the appliance, but estimation by means of total air flow predicts that the load on Prim_1 was about 19 kW and about 17 kW on Prim_2.

4.3. Effect of Secondary Air Reduction. The reduction of the secondary air supply was found to have generally negative effects on emissions: PM_1, alkali metals, and products of incomplete combustion. It is well-known that secondary air has a critical role in reducing emissions from biomass combustion. The staging of combustion air in primary and secondary zones has been found to have a major effect on emission formation during pellet combustion[16,19] by oxidizing the product of incomplete combustion in the secondary combustion zone. It has also been reported in batch combustion appliances, where CO emissions have been reduced by a factor of 2 or more[4,21] when a secondary air supply has been applied.

The effect of the secondary air supply on emission formation can be highlighted by comparing L_{25} to Sec_1 and Sec_2, where the primary air supply was constant during these tests but the secondary air supply changed. However, λ_{Prim} and λ_{Sec} changed because of the different air distribution and constant λ_{Tot} (Table 3). While the emissions from incomplete combustion were low in L_{25}, the emissions increased significantly on Sec_1 and Sec_2. The secondary air reduction particularly increased EC, OC, and CO emissions, but K and particle number emissions were also increased (Table 3). In these experiments, it seems probable that the secondary air supply also enhanced the fuel combustion rate because of the relatively small furnace, and thus, the decrease of secondary air flow simultaneously increased the λ_{Prim} because of the lower fuel combustion rate (Table 3). The increase of λ_{Prim} could have affected the formation of K particles in the fuel bed, leading to larger K emissions from Sec_1 and Sec_2 compared to L_{25}. Estimation by means of total air flow predicts that the loads of Sec_1 and Sec_2 were about 23 and 20 kW, respectively. Sec_1 emissions were similar to those of $L_{12.5}$ and L_7, but combustion conditions deteriorated from Sec_1 to Sec_2. OC emissions of Sec_2 can be affected by the DR, which was much higher than for the other experiments (Table 2). DR is known to affect the OC concentration, which contributes 10% of the total PM_1 emission from Sec_2.[29]

Sec_2 with the highest λ_{Prim} was practically the only experimental setting where particles over 1 μm were seen in mass size distributions. However, the lack of particles over 1 μm could have been generally affected by the appliance type over all test runs; most of the coarse particles in other experiments could have been stuck to the heat exchanger walls.

As already discussed for lower loads, the mixing and penetration of secondary air in the furnace can have a great impact on emission formation. Even though the secondary combustion air flows are much higher than for partial loads, it is possible that the inefficient mixing/penetration negatively affected the emission formation and the amount of oxygen and decreased the combustion temperature in the secondary combustion zone, which is indicated by the flue gas temperatures (Table 2).

4.4. Correlations between Air/Fuel Ratios and Emission Characteristics. The correlations between operational characteristics and emissions confirm that the air staging significantly affects the different emission properties in small-scale pellet combustion. λ_{Prim} and λ_{Sec} seem to affect emission properties, including both the formation of products of incomplete combustion and the emissions of alkali metal compounds. The strong correlations between $\lambda_{\mathrm{Prim}}/\lambda_{\mathrm{Sec}}$ and emissions indicate that the relation of primary and secondary air seems to be the most important factor affecting the different emission factors, and thus, it could be an important factor in emission control (Figures 5 and 6). It must be pointed out that these correlations also apply to partial-load conditions, whereas many other correlations found in this study correlated mostly when partial-load experiments were excluded from the test.

As mentioned earlier, the secondary air supply and λ_{Prim} seem to correlate with GMD (Figure 9). There might be different phenomena affecting the particle size. First, it seems that a higher particle concentration favored the increase of GMD by coagulation and agglomeration (Sec_1 and Sec_2). Coagulation and agglomeration can also be favored by longer residence times as was the case with partial loads ($L_{12.5}$ and L_7) with lower combustion air flows but with lower number emissions. Finally, it has been suggested that alkali metal particles are smaller than those of soot particles.[13] A low secondary combustion air supply seems to favor emissions with a higher level of EC (Table 3), whereas with high secondary combustion air, PM_1 was mainly composed of alkali metals (Prim_1 and Prim_2).

5. CONCLUSION

Particle and gaseous emission factors were found to vary according to load and air staging in the modern small-scale pellet boiler. However, the emissions were also relatively low in less optimal conditions when compared to other types of wood combustion appliances. PM_1 emissions were mainly composed of K and SO_4, and most of the increase that was seen in PM_1 emission factors between the different experiments was caused by an increase in EC emissions. At full load (L_{25}) and with a reduced primary air supply (Prim_1 and Prim_2), the PM_1 was mainly composed of ash particles.

Air staging was found to affect the emission formation in all of the experimental situations. Under partial-load conditions, the air/fuel ratio increased, air distribution changed, and more combustion air was led in through the primary air supply. This led to a slight increase in PM_1 emissions but to a more significant increase in CO emissions. Air staging on partial loads was nonetheless not optimal, and the emissions could be reduced by further optimization of air staging and furnace design.

Primary air reduction was found to decrease emission factors. PM_1 emissions decreased from 12.2 mg/MJ (L_{25}) to 5.9 mg/MJ (Prim_1) and 3.0 mg/MJ (Prim_2), and the emissions of EC and CO also decreased. The lowest emissions of K and SO_4 were found with reduced primary air supplies.

Sufficient input of secondary air together with good mixing is important to cut down the emissions. The reduction of secondary air led to increased emissions of unburnt gases and particles and a larger particle size.

The $\lambda_{\mathrm{Prim}}/\lambda_{\mathrm{Sec}}$ ratio was found to correlate with the emission factors of K, EC, PM_1, and CO, as well as with the release of K to fine particles. The $\lambda_{\mathrm{Prim}}/\lambda_{\mathrm{Sec}}$ ratio was found to affect not only the formation and oxidation of products from incomplete combustion but also the release of alkali metals. λ_{Prim} and λ_{Sec} were also found to correlate with the release of K to fine particles but not as well as the $\lambda_{\mathrm{Prim}}/\lambda_{\mathrm{Sec}}$ ratio. It can be concluded that, in this study, the $\lambda_{\mathrm{Prim}}/\lambda_{\mathrm{Sec}}$ ratio seems to be the most important operational factor affecting emissions from small-scale pellet combustion in different air-staging and load conditions.

According to the results obtained in this study, there are possibilities to further improve the combustion process by optimization of air staging to decrease emissions, particularly for partial loads but also under full-load conditions. In modern pellet boilers, where practically all of the PM_1 consists of ash particles, the reduction of the temperature in the fuel bed with optimizing primary air input seems to be the most promising method for primary emission reduction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Emission factors for the ash-forming content and content of individual metals (μg MJ^{-1}) of emitted PM_1. This material is available free of charge via the Internet at http://pubs.acs.org.

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Emission factors for the ash-forming content and content of individual metals (µg MJ^{-1}) of emitted PM$_1$.

	Ag	Al	As	B	Ba	Be	Bi	Cd	Co	Cr	Cu	Li	Mg	Mn	Mo
L_{25}	0.26	19.5	<DL	<DL	<DL	<DL	8.43	<DL	0.91	96.1	7.78	2.86	108	13.6	7.06
$L_{12.5}$	0.59	43.6	<DL	<DL	2.61	<DL	14.0	<DL	0.48	46.0	21.6	2.38	19.7	8.43	4.28
L_7	0.74	61.1	<DL	<DL	<DL	<DL	17.8	0.59	0.59	63.2	29.0	2.22	19.7	9.04	6.37
Prim_1	0.54	29.2	<DL	<DL	<DL	<DL	11.7	<DL	0.54	54.8	29.2	1.73	15.6	11.1	4.86
Prim_2	0.51	41.7	1.02	<DL	1.12	<DL	12.9	<DL	0.31	26.7	20.4	3.77	27.7	6.0	1.53
Sec_1	0.57	42.2	<DL	<DL	1.13	<DL	11.7	<DL	0.38	34.5	23.2	2.93	23.3	13.4	2.93
Sec_2	2.86	287	<DL	<DL	18.1	<DL	11.4	<DL	2.86	337	171	<DL	88.8	34.4	22.9

	Ni	Pb	Rb	Sb	Se	Sr	Th	Ti	Tl	U	V	Br	Cl	F	NO$_3$
L_{25}	62.8	1.82	14.4	<DL	<DL	<DL	<DL	8.17	0.13	<DL	<DL	<DL	<DL	<DL	372
$L_{12.5}$	28.7	12.4	13.4	0.36	<DL	<DL	<DL	8.67	0.12	<DL	<DL	<DL	<DL	<DL	<DL
L_7	42.8	6.67	12.9	<DL	<DL	<DL	<DL	7.56	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Prim_1	32.0	5.19	9.72	<DL	<DL	<DL	<DL	8.32	0.11	<DL	<DL	<DL	<DL	<DL	<DL
Prim_2	14.2	114	5.10	5.10	<DL	<DL	<DL	7.65	0.10	<DL	<DL	<DL	<DL	<DL	<DL
Sec_1	20.9	4.53	16.7	<DL	<DL	<DL	<DL	5.19	0.09	<DL	<DL	<DL	<DL	<DL	<DL
Sec_2	174.7	30.5	17.2	<DL	<DL	<DL	<DL	79.2	<DL	<DL	<DL	<DL	<DL	<DL	<DL

Paper II

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Physicochemical characterization of fine particles from small-scale wood combustion

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ABSTRACT

Emissions from small-scale wood combustion appliances are of special interest since fine particles have been consistently associated with adverse health effects. It has been reported that the physicochemical characteristics of the emitted particles affect also their toxic properties but the mechanisms behind these phenomena and the causative role of particles from wood combustion sources are still mostly unknown. Combustion situations vary significantly in small-scale appliances, especially in batch combustion. Combustion behaviour is affected by fuel properties, appliance type and operational practice. Particle samples were collected from six appliances representing different combustion situations in small-scale combustion. These appliances were five wood log fuelled stoves, including one stove equipped with modern combustion technology, three different conventional combustion appliances and one sauna stove. In addition, a modern small-scale pellet boiler represented advanced continuous combustion technology. The aim of the study was to analyze gas composition and fine particle properties over different combustion situations. Fine particle (PM_1) emissions and their chemical constituents emerging from different combustion situations were compared and this physicochemical data was combined with the toxicological data on cellular responses induced by the same particles (see Tapanainen et al., 2011). There were significant differences in the particle emissions from different combustion situations. Overall, the efficient combustion in the pellet boiler produced the smallest emissions whereas inefficient batch combustion in a sauna stove created the largest emissions. Improved batch combustion with air-staging produced about 2.5-fold PM_1 emissions compared to the modern pellet boiler (50.7 mg MJ^{-1} and 19.7 mg MJ^{-1}, respectively), but the difference in the total particulate PAH content was 750-fold (90 μg MJ^{-1} and 0.12 μg MJ^{-1}, respectively). Improved batch combustion and conventional batch combustion showed almost the same PM_1 emissions (51.6 mg MJ^{-1}), but a 10-fold difference in total particulate PAH emissions (910 μg MJ^{-1}). These results highlight that same PM_1 emissions can be associated with very different chemical compositions, potentially leading to different toxic properties of the particles. Thus, changing from an old, less efficient, combustion appliance to a modern appliance can have a greater impact on toxic properties than the emitted PM_1 mass might indicate.

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1. Introduction

Fine particles from small-scale biomass combustion are of special interest since they are consistently associated with adverse health effects. Exposure to fine particles has been associated with different health effects, such as pulmonary and cardiovascular symptoms (Kappos et al., 2004; Pope et al., 2002). Small-scale combustion of wood has been claimed to be a major source of fine particle mass, polycyclic aromatic hydrocarbons (PAHs) and some gaseous pollutants such as volatile organic compounds (VOC) (Hellén et al., 2008) and these emissions have been associated with adverse health effects (Straif et al., 2006; Naeher et al., 2007).

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The detrimental health effects, caused by particles are influenced by both the physical and chemical properties of the fine particles (Kocbach Bølling et al., 2009). These include particle-related size, surface area, chemical composition, solubility and structure.

In Finland, small-scale biomass combustion accounts for about 20% of all energy production (Mattila et al., 2003) and in 2000 it was estimated to be responsible for 25% of the total fine particle emissions (Karvosenoja et al., 2008). There are many different kinds of combustion appliances in households equipped with a wide range of different combustion technologies. Due to differences in combustion technology, usage and purpose of heating, combustion conditions vary between different appliances and combustion phases, and these can have a major impact on the emissions. For example, significant differences in particle emissions have been reported between conventional masonry heaters, modern masonry heaters and sauna stoves (Tissari et al., 2009).

Fine particles originated in small-scale wood combustion mainly consist of ash, elemental carbon and organic material (Tissari et al., 2008). Particle emissions are dominated by ash particles in good combustion, for example in pellet combustion. Ash particles are formed when ash species volatilize in the hot combustion chamber and form particles when the flue gas cools down. In small-scale combustion, the most common ash particles are alkali metals, such as K_2SO_4, KCl, K_2CO_3 and KOH (Sippula et al., 2007). Under poor combustion conditions, particles are mostly formed of elemental carbon and organic material (Tissari et al., 2008). In biomass combustion, incomplete combustion is invariably present regardless of the combustion conditions. Different kinds of hydrocarbons are also formed during incomplete combustion, including polycyclic aromatic hydrocarbons (PAH) that are known to be harmful to human health (Boström et al., 2002). Poor appliance design and different operational practices, e.g. poor quality of wood, overloading of the firebox or insufficient air supply may lead to incomplete combustion (Tissari et al., 2008).

Even though fine particles are a serious health concern, surprisingly little information is available about how different physicochemical properties of fine particles influence the toxicological responses. Since the health effects caused by poor air quality are the most important reasons to restrict and study fine particle emissions, it would be important to gather more information about formation of different particles in combustion processes when legislation is planned and improvements in technology introduced. It is also important to know how different particle properties emitted from different combustion situations are connected to their health-related properties.

In this study, fine particle and gaseous emissions from six different combustion appliances and combustion situations were studied. Five of these appliances were different batch combustion appliances, and one was a modern pellet boiler capable of continuous combustion. Batch combustion appliances represent both conventional and modern combustion technologies, and special combustion situations were selected for particle sampling. This selection was done to achieve a wide range of different combustion situations producing particles of different physicochemical properties. Since the combustion process is a complex phenomenon, and the temporary emissions are very difficult to define, the physicochemical characterizations were made over the specific combustion situations. Fine particle samples were collected so that they could be subjected to toxicological tests. The toxicological responses from the same particles are described by Tapanainen et al. (2011). The main focus was to investigate particles formed in different combustion situations under typical small-scale appliances, and to compare the findings to physicochemical properties and other particle properties.

2. Methods

2.1. Combustion appliances

Six different small-scale combustion appliances representing various combustion situations were studied. Five of these appliances were wood log fuelled combustion appliances, including one masonry heater equipped with modern combustion technology, three different conventional masonry heaters and one sauna stove. The modern small-scale pellet boiler represented modern continuous combustion technology. All of the combustion appliances, except for the pellet boiler, were typical small-scale appliances in use in Finland (Tissari, 2008).

The pellet boiler worked with a top-feed fuel input and had an integrated fixed grate burner and boiler. It was equipped with a lambda sensor and microprocessor controlled fans to provide combustion air. Pellet boiler represented efficient combustion (EFC). Three conventional masonry heaters represented conventional batch combustion (CBC). It is typical for the conventional masonry heaters that the inlet of combustion air, which draws in most of the combustion air, occurs through the grate though some part of the combustion air may also enter via the door of the heater without any precise control. In cases of conventional masonry heater 1 (CBC1) and conventional masonry heater 3 (CBC3), the appliances were relatively small masonry heaters (approx. 800 kg). In the case of conventional masonry heater 2 (CBC2), the appliance was relatively large (approx. 3500 kg) made of brick stones.

In the case of improved batch combustion (IBC), the appliance was a modern masonry heater made of soapstone. A modern masonry heater differs from its conventional counterpart in its air input principle i.e. both primary and secondary air is led to combustion chamber. Primary air is led through the grate, whereas secondary air is led to the top part of the combustion chamber from the sides, resulting in staged combustion. This has been found to improve the burnout of combustible gases and particles when compared to the situation with a traditional masonry heater (Tissari et al., 2009). The sauna stove was a light metal made traditional Finnish design which had a very simple combustion technology, where heat is stored in the small stones situated lying on top of the stove. Sauna stove represented inefficient batch combustion (IEBC), since it has been found to produce large emissions of PM_1, carbon monoxide (CO) and organic gaseous carbon (OGC) (Tissari et al., 2007, 2009). IBC/34, CBC2/F, CBC3/23 and IEBC/S include specific combustion situations that take place within the combustion cycles as they are described later in 2.4.

Gaseous and particle emissions from combustion appliances fluctuate significantly within combustion cycle according to combustion phases. This can be seen easily especially in batch combustion processes and they can be seen after every addition of the fuel. Combustion can be divided into three phases (Fig. 1). The firing phase (1) is defined as lasting from the ignition of the fire until the moment when the minimum O_2 is reached. The combustion phase (2) includes first a strong combustion which starts to die out as the amount of fuel decreases. The combustion phase is the period from the minimum O_2 concentration until a concentration of 14%. Burnout phase (3) is from that on (van Loo and Koppejan, 2008; Tissari, 2008). The variation over different combustion phases and combustion situations is highlighted in Fig. 1. However, in combustion appliances with continuous combustion, different combustion phases take place in the fuel layer, where combustion is stable and can be better controlled than in batch combustion appliances.

2.2. Appliance operation

Each of the combustion appliances was operated according to manufacturer's operation manual. In every combustion test, the

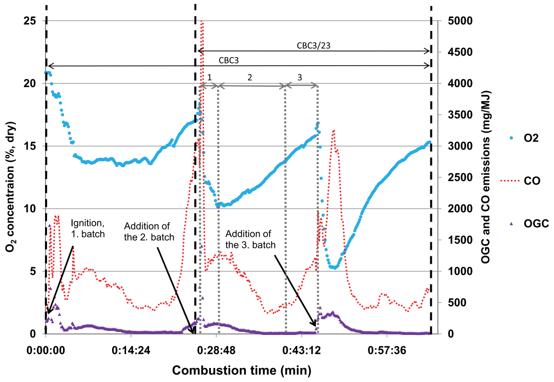

Fig. 1. Flue gas oxygen concentration, OGC emissions and CO emissions during combustion cycle in CBC3. Sampling periods, batch additions and combustion phases are presented. (1) Firing phase, (2) combustion phase and (3) burnout phase.

Table 2
Properties of the fuels used.

	Birch log	Pellet
Ash content (%)	0.4	0.3
Moisture (%)	10–13	8.1
NHV (MJ kg^{-1})	18.7	19.0
Al	0.32	0.76
Ca	313	892
Cr	0.07	<0.5
Cl	n/a	10
Cu	1	1.37
Fe	<200	44.3
K	527	420
Mg	35	142
Mn	81	82
Na	11	180
Ni	0.19	0.33
P	103	58
S	106	<0.02
Zn	48	<1

The elemental analyses are presented as mg kg^{-1} of dry fuel. The ash content is the mass percentage of dry fuel, and the moisture content is the mass percentage of wet fuel. NHV, net heating value; n/a, analysis result is not available.

appliance was initially at room temperature and it was left to cool down after previous test. An ignition batch, described in Table 1, was set on the bottom of the appliance's fire chamber, and 200 g of wood stick and chippings were placed on top of wood logs as kindling. The batch was ignited from top with matches. The pellet boiler was operated with nominal output power 25 kW. The boiler was set on 3 h before test to ensure stability of the system and stable combustion conditions. Birch wood was used in all of the log fuelled appliances with varying sizes of log batches with commercial wood pellet being used in the pellet boiler. The primary pellet raw material was pine. The fuel properties are presented in Table 2.

2.3. Experimental setup

Combustion tests were performed in a laboratory environment at stable temperature conditions. The experimental setup is presented in Fig. 2. The flue gases were led through an externally insulated steel stack and led outside through a hood using a flue gas fan. Particle samples to the diluters were taken from the stack through an insulated and externally heated (150 °C) sample line.

Sampling train consisted of three parallel dilution systems. A porous tube diluter (PRD) and ejector diluter (ED, Dekati Ltd.) (Lyyränen et al., 2004) were used for the rapid dilution of the samples for filter collections and there was also a Dekati Low Pressure Impactor (DLPI, Dekati Ltd.), which measured particle mass–size distribution. Aluminum foils, greased with a mixture of toluene and Apiezon-L vacuum grease (M & I Materials Ltd.) to prevent particle bouncing effect, were used in DLPI. PM$_1$ filter samples were collected on 47 mm polytetrafluoroethylene (PTFE) membrane filters (Pall Corporation, P/N R2PJO47) and 47 mm quartz fibre filters (Pallflex, Tissuequartz). A pre-impactor (Dekati Ltd.) with a cut-of-diameter of 1 µm was used to remove any particles with an aerodynamic diameter larger than 1 µm (Tissari et al., 2008). Filters were placed on stainless steel filter holders (Gelman Sciences Inc., model 2220). Dekati Gravimetric Impactor (DGI, Dekati Ltd.) with a 70 lpm flow rate and a cut-off size from 0.2 µm to 2.5 µm with backup filter was used for collecting PM$_1$ samples for chemical and toxicological analyses in each combustion situation. The dilution was carried out using a porous tube diluter. The DGI setup was the same as that used by Ruusunen et al. (2009). PTFE stages and backup filter were used in DGI. Approximately 30 mg of PM$_1$ sample was collected during three repeated tests for toxicological and chemical analyses (anions, cations and PAHs). Sample preparation is described in more detail in Tapanainen et al. (2011).

Dilution rations in PRD + ED system and in PRD in DGI systems were kept approximately the same in each test run. This was done to assure similar conditions and the same particle properties in two different dilution systems (Lipsky and Robinson, 2006). More

Table 1
Description of the combustion situations, appliances, sampling times and fuel.

		Description of situations	Combustion appliance	Collection time	Batch and fuel
EFC	Experiment 1, 4 tests	Efficient combustion	Pellet boiler	Continuous combustion, 2–3 h	Commercial wood pellet
IBC	Experiment 2, 3 tests	Improved batch combustion	Modern masonry heater	Cycle, 120 min	1. batch 10 × 0.4 kg, other batches 4 × 1 kg
IBC/34				3. and 4. batch, 50 min	
CBC1	Experiment 3, 3 tests	Conventional batch combustion	Conventional masonry heater 1	Cycle, 55 min	1. batch 7 × 0.23 kg, other batches 5 × 0.48 kg
CBC2	Experiment 4, 3 tests	Conventional batch combustion	Conventional masonry heater 2	Cycle, 140 min	1. batch 3 × 1 kg, other batches 3 × 1.3 kg
CBC2/F				Firing phase, beginning of the 2. batch, 15 min	
CBC3	Experiment 5, 3 tests	Conventional batch combustion	Conventional masonry heater 3	Cycle, 65 min	1. batch 7 × 0.43 kg, other batches 4 × 0.75 kg
CBC3/23				2. and 3. batches, 40 min	
IEBC	Experiment 6, 3 tests	Inefficient batch combustion	Sauna stove	Cycle, 55 min	1. batch 5 × 0.31 kg,
IEBC/S				Ignition batch and 2. batch, 20–35 min	2. batch 6 × 0.53 kg,
					3. batch 5 × 0.64 kg

About 200 g of kindling were used in the ignition in every combustion test. EFC, IBC, CBC1, CBC2, CBC3, IEBC include cycle with batch additions and ignition phases, which also take place in normal operation. IBC/34, CBC2/F, CBC3/23 and IEBC/S include specific combustion situations that take place within the cycles.

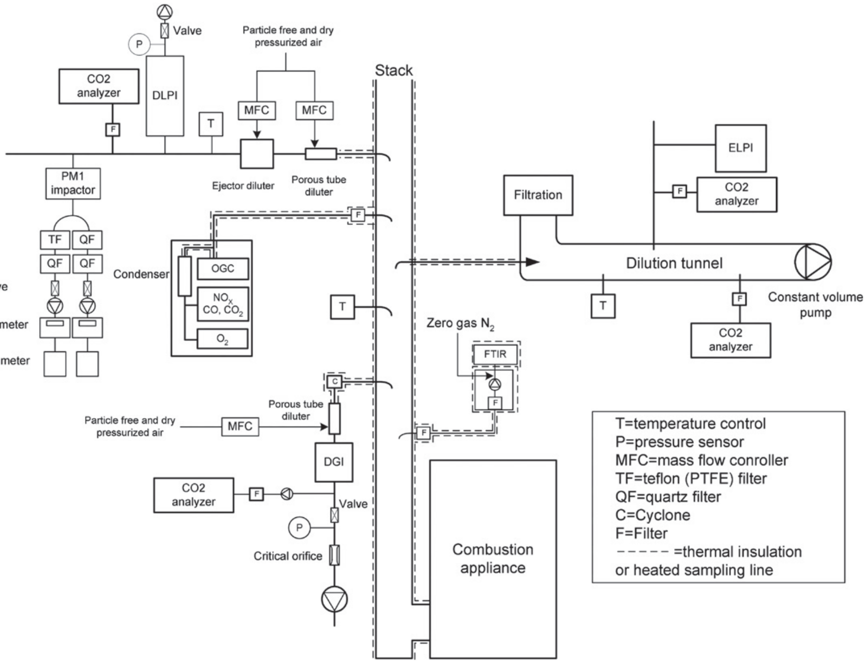

Fig. 2. Schematic drawing of the experimental setup.

dilution was provided for ELPI, since it oversteps more easily its detection area. Dilution ratios were calculated by using CO_2 concentration in the undiluted flue gas and in the diluted flue gas using the equation described by Sippula et al. (2009). Particle concentrations were dilution corrected by multiplying results with the dilution ratio. All of the emission results were calculated in relation to fuel energy input to the burning process (SFS 5624, 1990). The average dilution ratios calculated between 13.0 and 26.2 in PRD-DGI, between 13.9 and 25.5 in PRD + ED, and between 91 and 127 in the dilution tunnel (Table 3). A system of one PRD and two EDs was used in case of CBC2, because it was not possible to use a dilution tunnel due to the size and weight of the masonry heater. O_2 concentrations, presented in Table 3, varied between 8.1% with (IEBC) and 13.4% with (CBC1). Temperatures of the flue gas were measured continuously approximately 2 m after they entered into the chimney (Fig. 2). The lowest flue gas temperature was measured for CBC2/F, 90 °C and the highest flue gas temperature for IEBC, 450 °C. Diluted sample temperatures varied between 18 °C and 27 °C.

Particle number–size distributions were measured from dilution tunnel (ISO 8178-1, 1996) with Electrical Low Pressure Impactor (ELPI, Dekati Ltd.) with a flow rate of 10 lpm and a cut-off size from 24 nm to 9.38 μm with sintered impaction plates. Gaseous emissions, carbon dioxide (CO_2), carbon monoxide (CO), organic gaseous carbon (OGC) and nitrogen oxides (NO_X) were analyzed from undiluted flue gas by gas analyzer system (ABB, Cemas Gas Analysing Rack). Gas emissions were also measured with a Fourier Transform Infrared (FTIR, Gasmet Technologies Ltd.) gas analyzer. Carbon dioxide (CO_2) concentration was also measured continuously in diluted samples to calculate dilution ratios. CO_2 analyzers included three different CO_2 analyzers, one for the PRD-DGI system (ABB AO2040, Uras 14, ABB Automation GmbH), one in the dilution

Table 3
Dilution ratios, sample temperatures, flue gas temperatures and O_2 concentrations.

	O_2 (%)	Dilution ratio			Sample T, °C			Flue gas T, °C
		PRD + DGI	Dilution tunnel	PRD + ED	PRD-DGI	Dilution tunnel	PRD + ED	
EFC	11.9 ± 0.93	13 ± 4.3	106 ± 19	14 ± 1.3	24 ± 0.5	26 ± 0.6	20 ± 0.2	152 ± 1.2
IBC/34	10.5 ± 2.7	26 ± 9.3	810 ± 103[a]	24 ± 4.1	26 ± 0.5	27 ± 0.2[a]	27 ± 0.6	268 ± 18
IBC	11.6 ± 3.3		790 ± 130[a]			27 ± 0.5[a]		242 ± 61
CBC1	13.4 ± 3.6	16 ± 5.3	128 ± 27	24 ± 5.8	19 ± 0.5	22 ± 0.4	22 ± 0.8	222 ± 64
CBC2/F	8.4 ± 3.3	17 ± 3.6	280 ± 44[b]	35 ± 6.0	19 ± 0.5	26 ± 0.3[b]	23 ± 0.02	88 ± 8.0
CBC2	10.3 ± 4.0		385 ± 166[b]			24 ± 0.4[b]		96 ± 21
CBC3/23	12.2 ± 2.9	20 ± 4.5	91 ± 18	20 ± 2.8	23 ± 0.7	25 ± 0.2	21 ± 1.8	276 ± 45
CBC3	13.0 ± 3.0		88 ± 22			25 ± 0.3		246 ± 70
IEBC/S	10.9 ± 4.7	24 ± 13	90 ± 21	30 ± 10	19 ± 0.2	23 ± 0.9	19 ± 0.4	311 ± 100
IEBC	8.1 ± 5.0		108 ± 28			23 ± 1.2		450 ± 160

[a] Dilution ratio and temperatures were measured after dilution tunnel + ED.

[b] Dilution ratios and temperatures were measured after PRD + ED + ED. The values from continuous measurements are average values with standard deviations.

tunnel (Vaisala CARBOCAP, GMP343) and one after the PRD + ED system (Sensorex, SX 500, portable).

2.4. *Sampling for toxicological analyses*

Sampling times were selected to represent different kinds of combustion situations in normal small-scale combustion (Table 1). Selected combustion situations and their emissions may not represent typical average emissions from the types of appliances used in this study, but they merely represent the average values of emissions from different combustion situations. Combustion situations are affected by the appliance type, use of the appliance and fuel properties. Emissions over specific combustion situations can be related to the properties of the produced particles and their toxicological responses. However, particle number emissions and gas emissions are described both from the combustion cycle, as well as from each combustion situations (toxicological sampling time).

Sampling and collection times are divided into different categories according to the individual combustion situation in the different combustion appliances. The particle samples in EFC were collected from a small-scale pellet boiler with 25 kW maximum output power, which represented modern small-scale combustion technology. In CBC1, the sample collection period was 55 min over combustion cycle including the ignition phase and two batches. In CBC2 firing phase (CBC2/F), the sample time was 15 min from the beginning of the second batch to obtain a sample of PM_1 from a firing phase in conventional masonry heater. In CBC3 batches 2 and 3 (CBC3/23), the sample time was 40 min during second and third batches. It represented the relatively good combustion conditions in the CBCs. In IBC batches 3 and 4 (IBC/34), the collection time was 50 min during the third and fourth batches. In IEBC, sampling was conducted during the start (IEBC/S); ignition and the second batch.

2.5. *Chemical analyses*

All of the filter samples and impactor stages were weighed before and after particle collection in a stable room temperature and relative humidity around 20 °C and 40%, respectively. Filters were kept in the weighing room at least 24 h prior to weighing in order that they would stabilize. Gravimetric analyses were performed with a microbalance of 1 μg sensitivity (Mettler Toledo, MT5) with Staticmaster Po-210 charge eliminator from PTFE filters. PM_1 particle samples from DGI impactor stages were pooled together to form PM_1 sample for toxicological and chemical analyses (excluding OC/EC and gravimetric analyses). Detailed description of the sample preparation has been presented in detail in Tapanainen et al. (2011).

Carbonate carbon (CO_3), organic (OC) and elemental (EC) carbon analyses were performed from the quartz filter samples by a thermal-optical method (Turpin et al., 2000), using an OCEC Carbon Aerosol Analyzer (model 4 L) from Sun Laboratories Inc. The analyses were performed according to the National Institute for Occupational Health (NIOSH 1999) procedure. Detailed description has been presented by Sippula et al. (2007, 2009).

Concentrations of major inorganic ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) were analyzed using two Dionex ICS-2000 (Dionex Corporation, Sunnyvale, CA, USA) ion chromatography systems. Twelve different elements (Al, As, Cd, Co, Cu, Cr, Pb, Mn, Ni, Fe, Zn and V) were analyzed with an ICP-MS (Perkin-Elmer Sciex Elan 6000, Perkin-Elmer Corp., Waltham, MA, USA) using Rh as an internal standard (nitric acid and hydrofluoric acid dissolution).

2.5.1. *PAH analysis*

PAH compounds were analyzed by a method modified from Christensen et al. (2005) and Schubert et al. (2003); for details see Supplementary material. Briefly, PAH compounds in particulate matter samples were identified and quantified comparing against a mixture of standard compounds comprising of 30 commercially available PAHs. In addition, deuterated PAH compounds (product Z-014J, AccuStandard Inc., USA) were used as an internal surrogate standard for quantification of the PAHs. To evaluate and validate the analytical method, a Standard Reference Material (SRM 1649a Urban Dust, NIST, Gaithersburgh, USA) was analyzed in a similar manner to samples. The particulate matter samples were spiked with the internal surrogate standard and extracted with dichloromethane in an ultrasonic bath. Solid-phase extraction (Alumina-B, ICN Biomedicals, Germany) was used as a cleanup step before injection of the sample on the GC–MS system (Agilent). Quantification limit was estimated by signal-to-noise ratio and the average quantification limit was 0.1 ng mg^{-1}.

3. Results and discussion

3.1. *Gaseous emissions*

3.1.1. *Gaseous emissions during the combustion situations*

Gaseous emission factors varied significantly between the different combustion situations. The emissions values from continuous measurements are presented as an average of all measured data during the sampling period. Since the combustion process in batch combustion changes significantly over time, the presented standard deviation also describes the variation in the process. The largest emission factors were seen in IEBC/S, with the smallest in EFC (Table 4). In IEBC/S, the emissions of CO and OGC were 4400 mg MJ^{-1} and 830 mg MJ^{-1}, respectively. CO and OGC

Table 4
The averaged gaseous emission factors (mg MJ^{-1}).

	CO	OGC	NO_x	HCl	CH_4	C_6H_6
EFC	80 ± 67	0.96 ± 1.3	49 ± 7.0	0.1 ± 0.1	0.3 ± 0.2	0.9 ± 1.4
IBC	580 ± 490	16 ± 59	74 ± 47	n/a	n/a	n/a
IBC/34	390 ± 270	14 ± 45	75 ± 11	n/a	n/a	n/a
CBC1	2700 ± 2100	95 ± 260	82 ± 79	1.7 ± 8.2	47 ± 130	7.0 ± 36
CBC2	2300 ± 330	250 ± 530	194 ± 250	0.8 ± 20	130 ± 280	27 ± 87
CBC2/F	1200 ± 1100	82 ± 102	76 ± 22	1.3 ± 3.0	84 ± 120	18 ± 37
CBC3	830 ± 810	66 ± 210	82 ± 55	1.0 ± 1.4	43 ± 57	5.9 ± 7.0
CBC3/23	930 ± 840	94 ± 200	88 ± 40	0.9 ± 0.7	55 ± 64	6.9 ± 6.8
IEBC	6100 ± 7400	1050 ± 1500	540 ± 670	n/a	n/a	n/a
IEBC/S	4400 ± 5600	830 ± 1200	420 ± 540	3.2 ± 5.8	770 ± 1200	50 ± 87

CO, OGC and NO_x were measured with the ABB analyzing rack, while HCl, CH_4, C_6H_6 were measured with the FTIR. The values from continuous measurements are average values with standard deviations.

emissions in EFC were 79 mg MJ^{-1} and 0.96 mg MJ^{-1}, respectively. This highlights the differences between good continuous combustion in EFC and incomplete combustion in IEBC/S. Gaseous emissions were similar to each other in different CBCs. CO emissions were the highest in CBC1, about double to CBC2/F and CBC3/23. However, OGC emissions were on a similar level in all of CBCs. Emissions of CO and OGC were lower in IBC/34 than in CBCs. Since the appliances and batch arrangements are very similar in CBC3/23 and IBC/34, but CBC3/23 without air-staging, the results are well comparable with each other. This shows that the air-staging used in IBC decreases the gaseous emissions due to better burnout of combustible gases.

3.1.2. *Gaseous emissions during combustion cycles*

Comparing these results from the combustion cycle to the ones described earlier in chapter 3.1.1, the comparison of the selected combustion situations can be compared to combustion cycles (Table 4). In CBC1 and EFC, the emissions described earlier already represent combustion cycles. All of the gaseous emission factors in CBC2/F were clearly lower than the emissions emerging from CBC2. On the other hand, in CBC3, the emissions were slightly higher, than in CBC3/23 for the same appliance. Compared to results from previous study (Tissari et al., 2009) obtained from similar combustion situations and combustion appliances, the CO results here are larger from CBC1 and CBC2, but smaller in CBC3. It seems that the appliance design in CBC3 was optimal for burnout of combustible gases compared to CBC1 and CBC2. CO and OGC emissions from IEBC were approximately two times larger than that reported previously in a sauna stove (Tissari et al., 2009), but similar results have been reported from an old-type wood boiler (Johansson et al., 2004). Large emissions can be explained by the differences in appliance usage and with the simple combustion technology. In addition, the gaseous emissions (CO and OGC) in IBC are about half of the emissions described before in a masonry heater equipped with air-staging (Tissari et al., 2009).

3.2. *Particle emissions*

3.2.1. *PM$_1$ emissions during the toxicological sampling*

PM$_1$ emission factors can be divided into three main groups, emissions from inefficient batch combustion (IEBC), emissions from batch combustion (CBC1, CBC2, CBC, IBC) and emissions from efficient combustion (EFC) (Table 5). The emissions varied less within each specific group than between the different groups. From IEBC/S, the PM$_1$ emission was highest, 260 mg MJ^{-1}. The lowest PM$_1$ emission originated from EFC 19 mg MJ^{-1}, as expected. PM$_1$ emissions from the different masonry heaters did not vary significantly, between 51 mg MJ^{-1} in IBC/34 and 81 mg MJ^{-1} in CBC1, even though the appliances and combustion situations were different. It has also to be noted that although the PM$_1$ emissions from IBC/34 and CBC3/23 were rather similar, CO emission from CBC3/23 was 1.6-fold and OGC emission 5.9-fold compared to IBC/34.

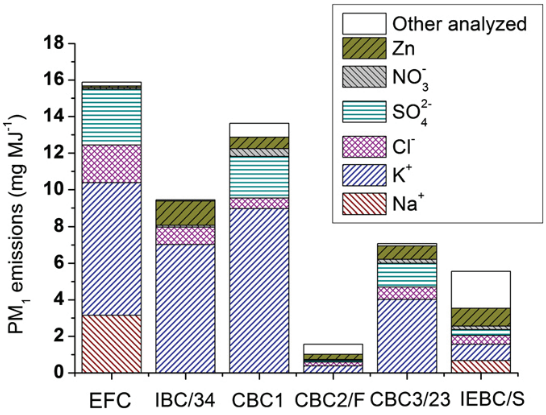

Fig. 3. Emissions of PM$_1$ ash compounds.

3.2.2. *PM$_1$ chemical composition*

Most of the particulate matter consists of inorganic alkali metal components in EFC, shown in Fig. 3 and Table 6. The most abundant chemical species were K$^+$, SO$_4^{2-}$, Cl$^-$ and Na$^+$. These components vaporize in hot flame temperatures from ash-forming elements in the fuel. When flue gases cool down, they form particles (Valmari et al., 1998). Combustion in EFC differs significantly from CBCs and demonstrated in the results presented in Fig. 3 and Tables 5 and 6. EC is the most abundant component in all of the CBCs and IBC/34 highlighting incompleteness of the oxidation in batch combustion appliances (Wiinikka, 2005; Tissari et al., 2007). Other common components are OC, K$^+$, CO$_3$ and SO$_4^{2-}$. The smallest emissions of such components were seen in CBC2/F. When considering these results in conjunction with previous studies it can be concluded that its combustion temperature was most likely the lowest of all appliances tested here, since the evaporation of these components is strongly related to combustion temperature (Davidsson et al., 2002; Knudsen et al., 2004). However, the temperature inside the combustion chamber was not measured. OC is a typical component of all kinds of batch combustions where incomplete combustion is always present (Tissari et al., 2007). Interestingly, the PM$_1$ chemical properties are similar with IBC/34 and CBC3/23, even though the air-staging in IBC clearly affected the gas emissions. This shows that the air-staging in IBC did not affect the oxidation of OC and EC significantly. In IEBC/S, EC and OC are the most abundant components in the particle phase (Table 5). This confirms the hypothesis that with simple combustion technology and ignition phase of the

Table 5
Emission factors of PM$_1$, carbon compounds, number emissions, and mean particle sizes.

	PM$_1$	EC	OC	CO$_3$	N_{Tot}	GMD	MMD
EFC	19.7 ± 1.6	0.1 ± 0.17	0.9 ± 2.1	1.2 ± 1.1	3.5E + 13 ± 8.0E + 12	60 ± 3.3	137 ± 6.1
IBC					8.4E + 13 ± 7.2E + 13	76 ± 11	
IBC/34	50.7 ± 26	24 ± 6.7	3.6 ± 1.2	2.3 ± 0.50	6.8E + 13 ± 3.5E + 13	74 ± 5.1	179 ± 25
CBC1	81.4 ± 13	24 ± 5.3	11 ± 4.6	3.4 ± 2.3	1.0E + 14 ± 1.8E + 14	63 ± 10	277 ± 110
CBC2					1.2E + 13 ± 2.1E + 13	142 ± 53	
CBC2/F	67 ± 6.5	49 ± 10	19 ± 16	4.2 ± 7.3	1.9E + 13 ± 3.6E + 12	136 ± 32	658 ± 230
CBC3					3.1E + 13 ± 2.2E + 13	70 ± 11	
CBC3/23	51.6 ± 12	28 ± 3.4	3.5 ± 1.5	5.4 ± 3.0	3.4E + 13 ± 1.4E + 13	73 ± 9.2	186 ± 14
IEBC					7.3E + 13 ± 4.4E + 13	107 ± 60	
IEBC/S	257 ± 85	130 ± 23	160 ± 26	5.9 ± 12	6.7E + 13 ± 3.2E + 13	105 ± 58	415 ± 83

PM$_1$, EC, OC, CO$_3$, mg MJ^{-1}; N_{Tot}, # MJ^{-1}; GMD and MMD, nm. The values from continuous measurements (N_{Tot} and GMD) are average values with standard deviations.

Table 6
Emission factors for the ash-forming content (mg MJ^{-1}) and content of individual metals (µg MJ^{-1}) of emitted PM$_1$.

	EFC	IBC/34	CBC1	CBC2/F	CBC3/23	IEBC/S
Na$^+$, mg MJ^{-1}	3.2	<DL	<DL	9.5E-03	<DL	0.67
NH$_4$$^+$, mg MJ^{-1}	8.1E-03	<DL	<DL	0.098	0.022	<DL
K$^+$, mg MJ^{-1}	7.2	7.0	9.0	0.37	4.0	0.89
Mg^{2+}, mg MJ^{-1}	<DL	1.8E−03	<DL	8.2E-03	3.1E-03	<DL
Ca^{2+}, mg MJ^{-1}	<DL	0.015	8.8E-03	0.049	0.024	<DL
Cl$^-$, mg MJ^{-1}	2.1	0.95	0.58	0.22	0.67	0.49
SO$_4$$^{2-}$, mg MJ^{-1}	3.1	<DL	2.3	0.093	1.3	0.32
NO$_3$$^-$, mg MJ^{-1}	0.079	0.11	0.43	0.044	0.22	0.19
Cd, µg MJ^{-1}	0.17	3.1	2.2	1.8	1.8	1.9
Co, µg MJ^{-1}	<DL	14	3.2	5.5	1.4	<DL
Cr, µg MJ^{-1}	0.4	<DL	1.7	0.026	<DL	1.5
Cu, µg MJ^{-1}	6.5	5.5	5.9	1.7	2.0	<DL
Mn, µg MJ^{-1}	20	2.7	7.4	43	1.9	<DL
Ni, µg MJ^{-1}	<DL	0.62	0.81	1.6	0.7	<DL
Pb, µg MJ^{-1}	3.9	11	12	2.7	7.2	6.3
V, µg MJ^{-1}	<DL	0.021	<DL	0.11	0.026	0.10
As, µg MJ^{-1}	0.045	<DL	<DL	<DL	0.037	<DL
Fe, µg MJ^{-1}	1.4	20	21	160	24	<DL
Zn, µg MJ^{-1}	84	1300	630	280	730	970

<DL, below detection limit.

combustion (ignition and 2. batch), the particles are mostly formed of components from incomplete combustion. However, Na$^+$, Cl$^-$, K$^+$, SO$_4$$^{2-}$ and Zn could also be identified from IEBC/S particles, but in a small fraction.

3.2.3. *PAH emissions*

PAH contents of PM$_1$ from IEBC/S and EFC can be clearly distinguished from the other situations, IEBC/S with the largest and EFC with the smallest PAH contents (Table 7). Different combustion situations in CBCs are at a similar level in total PAHs, but the differences between IBC/34 and different CBCs were greater than in PM$_1$. In addition, when comparing PAH contents and PM$_1$ emissions from IBC/34 and EFC, it can be seen that the difference in PAHs between these two combustion situations are greater than indicated by the PM$_1$ emissions. This highlights that the impact of improved combustion technology on the particulate PAH seem to be more significant than would be predicted from the PM$_1$ emissions, gas emissions or other particle chemical properties. This has importance from legislative point of view, where PM is commonly used as restricted factor. Similar findings on PAHs from batch combustion appliances with different combustion technologies (Tissari et al., 2007) and differences between old and new combustion technology (Johansson et al., 2004) have been reported previously. PAH emissions in this study, are similar to those described elsewhere in similar combustion situations (Hytönen et al., 2009; Boman et al., 2005), despite slightly different collection methods and dilution ratios used in these studies. Hytönen et al. (2009) analysed 15 different PAH compounds and Boman et al. (2005) 37 different PAH compounds. Total PAHs from combustion cycle in masonry heater (CBC1) are about 2-fold from a masonry heater and total PAHs from IEBC/S produced about 2-fold emissions compared to smouldering combustion in Hytönen et al. (2009). Boman et al. (2005) described higher total PAH emissions from a pellet boiler than the ones here in EFC in similar combustion situations, but overall, both emissions are low.

The distributions of the different PAH-species varied with the different combustion situations. In all combustion situations, phenanthrene, fluoranthene and pyrene were the most common PAH compounds, except in CBC3/23 where cyclopenta[c,d]pyrene was the third most common PAH compound. Thus prevalence of the three most common PAH compounds, phenanthrene, fluoranthene and pyrene, has also been described by Boman et al. (2005). In EFC with smallest amount of total PAHs, about 73% of PAHs were phenanthrene, fluoranthene and pyrene. In IBC, the amount was 77%, 32% in CBC3/23, 42% in CBC2/F, 41% in CBC1 and 50% in IEBC/S.

Table 7
Polycyclic aromatic hydrocarbon (PAH) contents in PM$_1$ samples, total PAHs, genotoxic PAHs and PAH/PM$_1$.

PAH compounds, ng mg^{-1} in PM$_1$	EFC	IBC/34	CBC1	CBC2/F	CBC3/23	IEBC/S
Naphthalene	0.2	1.0	1.1	<DL	<DL	5.7
Acenaphthylene	<DL	4.5	51.1	129.3	11.9	1517.7
Acenaphthene	<DL	<DL	1.6	3.5	1.4	64.5
Fluorene	<DL	4.9	90.0	333.5	34.6	2928.6
Phenanthrene	0.6	352.5	2317.3	5369.6	1060.8	19381.1
Anthracene	<DL	25.6	483.7	955.7	226.5	4611.7
1-Methylphenanthrene	0.1	15.7	148.0	122.9	81.8	788.4
Fluoranthene	1.7	412.1	2834.9	3475.9	2187.4	11264.9
Pyrene	2.1	371.2	2742.1	3199.8	2578.2	12045.6
Benzo[c]phenanthrene	0.1	31.9	29.9	361.2	248.8	875.8
Benzo[a]anthracene	0.1	46.1	1004.3	1396.5	1051.8	3005.7
Cyclopenta[c,d]pyrene	0.2	<DL	2150.1	1991.1	1954.2	6576.1
Triphenylene	0.1	5.3	127.7	187.2	85.6	366.0
Chrysene	0.1	19.1	907.0	1201.9	908.7	2493.0
5-Methylchrysene	<DL	0.7	7.4	7.3	4.5	18.5
Benzo[b]fluoranthene	0.1	47.7	783.2	1208.4	859.7	1748.1
Benzo[k]fluoranthene	<DL	5.0	1120.5	868.0	656.8	4497.0
Benzo[j]fluoranthene	0.1	19.3	365.9	881.3	626.4	927.5
Benzo[e]pyrene	0.2	31.2	524.8	801.3	600.3	1234.2
Benzo[a]pyrene	0.1	32.6	1149.0	2001.9	1628.4	3245.0
Perylene	<DL	4.2	152.9	255.4	216.8	438.8
Indeno[1,2,3-cd]pyrene	<DL	11.5	506.9	924.1	703.7	1305.5
Dibenzo[a,h]anthracene	<DL	1.7	49.5	156.3	122.2	210.2
Benzo[g,h,i]perylene	0.2	16.1	669.4	1051.2	924.6	1672.8
Anthanthrene	<DL	2.3	307.9	549.7	473.0	1006.9
Dibenzo[a,l]pyrene	<DL	<DL	4.0	26.0	11.9	13.0
Dibenzo[a,e]pyrene	<DL	<DL	63.3	190.5	93.4	208.8
Coronene	<DL	1.5	421.8	419.3	245.3	971.0
Dibenzo[a,i]pyrene	<DL	<DL	<DL	53.1	21.1	<DL
Dibenzo[a,h]pyrene	<DL	<DL	12.2	92.6	26.8	19.7
Total PAHs	5.96	1464	19027	28215	17647	83442
Total genotoxic PAHs	2.62	650	10400	14070	10273	33241
PAH/PM$_1$ (%)	6.0E-04	0.15	1.9	1.8	2.8	8.3
Proportion of genotoxic PAHs from the sum of all PAHS	0.439	0.444	0.547	0.499	0.582	0.398

Genotoxic PAH compounds defined on the basis of the WHO/IPCS criteria (WHO, 1998). Determination limit of the method 0.1 ng mg^{-1}. < DL, under determination limit.

Total PAH emissions from PM$_1$ emissions (PAH/PM$_1$) ranged extensively, the lowest value being 0.00006% for EFC and the highest was 8.3% for IEBC/S. PAH/PM$_1$ described by Boman et al. (2005) with a different types of pellet combustion are higher than those detected in here. However, similar to Boman et al. (2005), it was seen also here that the PAH/PM$_1$ decreased as the emissions of OGC and total PAHs became smaller. In addition, OGC emissions seem to correlate with total PAH emissions, but due to the small number of values, no conclusions could be made. The total genotoxic PAHs were calculated as a percentage of the total PAH, as described by Jalava et al. (2005) (Table 7). Genotoxic PAHs represent 38% (IEBC/S) to 58% (CBC2/F) of total PAHs.

3.2.4. *Particle size distributions*

The mass–size distributions are presented in Fig. 4 and mass mean diameters (MMD) in Table 5. IEBC/S can be clearly distinguished from other distributions. The emission is clearly higher and the MMD is larger (415 nm), while MMD is 277 nm in CBC1 and 137 nm in EFC. The differences between different combustion situations for mass–size distributions are much clearer than for number–size distributions (Fig. 5). IEBC/S can be clearly distinguished, and there is no bimodal distribution compared to number–size distribution. One must

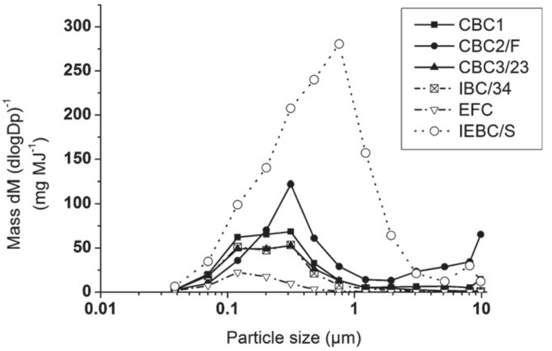

Fig. 4. Mass–size distributions from the combustion tests under different combustion situations, measured with DLPI.

remember that mass–size distributions were measured over specific combustion situations and they represent averaged values over certain time periods.

The averaged number emission factors (N_{Tot}) and geometric mean diameters (GMD) over combustion situations are presented in Table 5. GMD values calculated from ELPI data varied between 61 nm and 136 nm. The largest GMD values were measured from CBC2/F and the smallest from EFC. On the other hand, the number emission was smallest in CBC2/F, 1.9E + 13 #/MJ. The highest number emission was measured from CBC1, 1.0E + 14 #/MJ. The Fig. 5 shows IEBC/S and CBC2/F bimodal number–size distributions in IEBC/S and CBC2/F. These two combustion situations are also those with the most incomplete combustion, according to the emissions of gases, EC and OC. It has been previously reported that particle size increases when combustion situation deteriorate (Tissari et al., 2008). In CBC2/F, the low flue gas temperature (Table 3) provides also evidence that the residence time inside the appliance has been relatively long, giving the particles more time for coagulation/agglomeration, leading to a smaller number concentration and a larger particle size (Table 5).

3.3. Particle size properties and number emissions in combustion cycles

The averaged number emission factors and GMDs during the combustion cycles are presented in Table 5. The number emissions varied between 1.2E + 13 #/MJ in CBC2 and 8.4E + 13 #/MJ in IBC. The average GMDs varied from 70 nm in CBC3 to 142 nm in CBC2. It has been studied before that the number emissions and particle sizes fluctuate significantly during the combustion process, especially in batch combustion appliances. Only averages are presented here, but a detailed description with similar appliances can be found in Tissari et al. (2007).

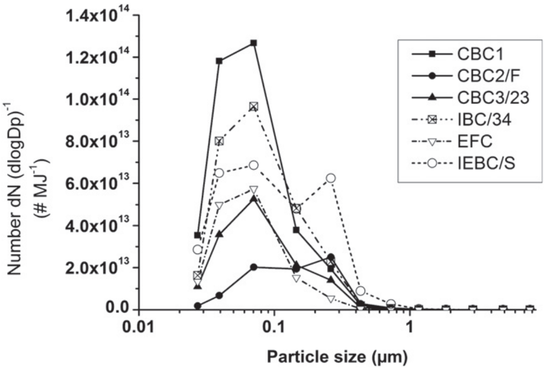

Fig. 5. Number–size distributions from the combustion tests under different combustion situations, measured with ELPI.

4. Conclusions

The results presented in this study clearly show that substantial differences in fine particle properties were produced by the different combustion situations from small-scale appliances. It is evident that PM_1 mass does not reflect all of the variation affecting possible toxic properties of fine particles originating from combustion. The physicochemical properties of the particles produced here represented very different combustion situations but this reflects well the situation with small-scale combustion appliances operated in different ways for different periods of time. This gave us a possibility to study the effect of combustion situations on particle physicochemical properties. It must be pointed out that the particle properties and particle emissions described here do not necessarily represent typical emissions of the appliance type, but rather the particle properties originating under these specific combustion situations.

Log fired batch combustion with simple combustion technology in IEBC/S produced the largest PM_1 emissions, whereas a modern pellet fired continuous combustion appliance in EFC created the smallest emissions. The differences between different batch combustion situations in different masonry heaters, however, were more or less at the same level, even though it was predicted from the gas emissions that they would more significantly differ from each other. It was expected that at least the IBC/34 with its air-staging would produce smaller PM_1 emissions and that particle chemical properties would differ more from CBCs. However, if one considers only the particle chemical properties, the differences between different CBCs were very small. The only clear difference was in CBC2/F where the gas emissions already revealed more incomplete combustion and this was reflected in the amount of OC and EC. As combustion conditions improve, larger fractions of K^+, SO_4^{2-} and some Cl^- are analyzed from the fine particles. In good continuous combustion, fine particles are mainly formed from different alkali metals K^+ and Na^+, and also Cl^- and SO_4^{2-}. In IBC/34, these same elements became more prevalent, but the presence of particles of EC and OC show that there are more areas of incomplete combustion in the combustion zones of this application than in pellet boiler.

No straightforward correlations were found between different combustion situations with particle number emissions and GMD. It has been previously shown that particle size will decrease and number emission increase, as combustion conditions improve (Tissari, 2008). The bimodal distribution in the particle number–size distributions and larger particles sizes were observed in those cases where combustion conditions deteriorated. The ultrafine particle mode has been proposed to be mainly formed of ash particles and the shift of the particle size during different combustion conditions to be formed from condensed organic vapour. We believe that this explains the differences between particle sizes and compositions also in this study.

Substantial differences were seen in PAH emissions between different combustion situations. As PAHs are known to be harmful to human health, it can be predicted that these results would be reflected in the toxic potencies of fine particles. When the fine particle emissions from modern and conventional masonry heaters were compared, it can be seen that PM_1 emissions were roughly similar but the difference in PAHs was 10-fold. These results show that PAH emissions can decrease dramatically when air-staging is applied in the batch combustion technology. In addition, even though a log fired sauna stove in IEBC/S is not a widely used combustion appliance in other parts of the world, its possible health effects seem to be significant, at least on the local scale, since the PAH emissions from this device are more than 10 times higher than those from CBCs. This applies to any incomplete combustion process as well. Therefore, it should be possible to decrease PAH emissions rather easily by improving the combustion technology.

Different combustion situations produce different kinds of particle emissions and particles with different physicochemical characteristics. It is clear that incomplete combustion produces more emissions than combustion under more optimal conditions, but the differences in all health-related chemical components can be greater than the PM_1 alone would indicate. More care should be taken in the design of combustion appliances, and improving combustion technology in small-scale batch combustion appliances. In addition, a wider set of chemical analyses is recommended to be performed in order to provide more specific data to aid in the evaluation of health effects attributable to small-scale combustion of wood.

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Appendix. Supplementary material

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PAH compounds in particulate matter samples were identified and quantified comparing against a mixture of standard compounds comprising of 30 commercially available PAHs. Reference PAH compounds investigated in this study were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). An internal surrogate standard was used for quantification of the PAH. Standard reference material, SRM 1649a Urban Dust (NIST; Gaithersburg, MD, USA), was used for evaluation and validation of the analytical method. Hexane and dichloromethane were used as solvents (HPLC grade, Rathburn Chemicals, UK).

5 or 10 mg of PM samples that were sampled during the specific combustion situations, were spiked with the internal surrogate standard of deuterated PAHs and extracted in Kimax glass tubes with 3 ml of dichloromethane for 15 min using an ultrasonic bath (model USC1200TH, VWR). After the extraction, a few drops of nonane, were added and the solvent volume was reduced to approximately 100 µl under a gentle stream of nitrogen and solvent exchanged to hexane. Solid-phase extraction was used as a cleanup step before injection of the sample on the GC-MS system. SPE columns were prepared for activated Alumina-B (ICN Biomedicals, Germany). The columns were conditioned with 6 ml of hexane before addition of the sample. Sample extracts were loaded on top of the column and eluted with 8 ml of hexane to remove aliphatic fraction. The PAH fraction was eluted with 10 ml of dichloromethane and concentrated to approximately 100 µl.

GC-MS analysis were performed on a gas chromatograph (6890N GC, Agilent) coupled to a mass-selective detector (5973inert MSD, Agilent). The GC column used for analyses was a 50 % phenyl methylpolysiloxane (DB-17ms, 60 m × 0.25 mm i.d. × 0.25 µm film thickness, J&W Scientific) with a 10 m retention gap (0.25 mm i.d.). Pulsed splitless injection was used with injection pressure 350 kPa for 1 min after the 2 µl sample injection. The injector temperature was held at 320 °C. The GC carrier gas was helium (1.2 l/min). The initial GC temperature, 60 °C, was held for 1 min then programmed at 6.5 °C min^{-1} to a final temperature of 320 °C, which was held for 49 min. Total run time was 90 min. Transfer line temperature was set to 320 °C. The MSD was operated in electron ionization mode and the temperatures of the MSD ion source and quadrupole analyzer were kept at 230 °C and 150 °C, respectively. Quantitative analysis was performed in the selected ion monitoring mode. The quantification limit was estimated via the signal-to-noise ratio and the average quantification limit was 0.1 ng mg^{-1}. Blank samples were also cleaned and analyzed at the same time as the PM samples to check for potential contamination.

Paper III

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Fine Particle and Gaseous Emissions from a Small-Scale Boiler Fueled by Pellets of Various Raw Materials

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ABSTRACT: The market of pellet fuels has undergone drastic changes in Europe in recent years. Traditional raw materials have become inaccessible due to unavailability or dramatic increases in prices. It is possible to use other feasible raw materials for pellet production. However, novel raw materials can have disadvantages with respect to usability and emissions, and these issues need to be considered before such raw materials are taken into wide-scale production. Such factors are especially important in small-scale pellet combustion. Fine particle and gaseous emissions from 21 pellet fuels of various raw materials were studied in a residential pellet boiler. These fuels represented a wide range of stem wood, bark, and forest residues from different tree species, as well as peat, agricultural biomass, and different mixtures of these. Fuel characteristics, fine particle mass (PM_1) emissions, number emissions, number size distribution, PM_1 chemical composition, and the main gaseous emissions were measured. The smallest PM_1 emissions were measured from peat pellets, followed by wood-peat pellets and woody biomass pellets containing only small amounts of bark. Peat also reduced the PM_1 and CO emissions when blended with woody biomass pellets. Pellets containing bark produced clearly higher PM_1 emissions due to the higher content of ash-forming elements, such as potassium, chlorine, and sodium, in the fuels. The highest PM_1 emissions were seen with straw pellets. Linear correlations were found between emissions and fuel characteristics: fuel K content, fuel K+Na+Cl content, and fuel (Na+K)*2Cl/S molar ratio being the most important parameters. The results show that biomass raw materials significantly affect particle emissions in combustion. The addition of peat to biomass can result in lower particle emissions but higher emissions of SO_2 and HCl.

1. INTRODUCTION

Residential heat production with pellet fuels is an interesting alternative to fossil fuels, such as oil, which can be replaced with pellets rather easily. However, the pellet market in Europe has faced problems with rapidly increasing demand[1] resulting in a lack of raw materials[2] for pellet production. Furthermore, production of liquid biofuels in recent years has started to compete for the materials previously used for pellet production. The change to a wider assortment of raw materials brings new challenges, which need to be considered when the materials are taken into use. At the same time, the EU has set targets to increase the use of biomass in energy production, which can include an increase in the use of pellets.[3]

Pellets can be used in both residential combustion and in large combustion plants.[4] Alternative pellet raw materials have certain characteristics which make their use more challenging compared to normal wood pellets, especially in residential use. Alternative materials often have relatively high ash contents and different compositions of ash forming elements compared to conventional pellet raw materials.[5] The ash content in commercial pellets is usually under 0.5% but can increase to over 15% in pellet fuels made of agricultural biomass.[5] High ash content and especially a high alkali metal concentration in a fuel typically leads to high fine particle emissions.[6] Furthermore, alkali metals in combination with silicates or phosphorus can lead to the problems of ash melting and sintering in the furnace. These topics have been widely discussed elsewhere.[7−11]

Particle emissions from small-scale combustion are usually dominated by fine particles (PM_1), which are in the size class under 1 μm.[12−15] The formation of fine particles in combustion has several disadvantages; in boilers they participate in fouling and corrosion of heat exchangers,[16] are harmful to health when released to ambient air,[17,18] and affect the climate system in several ways.[19,20] The emissions from biomass combustion contain species released from the fuel, such as ash particles, nitrogen oxides, and sulfur dioxide and species formed due to incomplete combustion, such as carbon monoxide (CO), organic gaseous compounds (OGC), elemental carbon (EC), and organic material. However, particle emissions from automated pellet combustion processes are mainly comprised of ash species, and the proportion of species from incomplete combustion is low.[21,22]

Fine particle emissions from continuously fired biomass combustion systems are mainly comprised of alkali metal sulfates, chlorides, and carbonates.[16,23] Potassium is known to have a key role in the formation of fine particles. K_2SO_4, KCl, and K_2CO_3 have been found to be the most common fine particle components in biomass combustion[16,23] and in residential pellet combustion appliances.[6] Other important species are Na, S, Cl, and Zn. The behavior of Na is similar to K, while Zn is mainly found as ZnO and $ZnCl_2$ in fine particle emissions.[24] The ash content and composition of wood fuel has been shown to affect the fine particle emissions during combustion. The sum of K, Na, Cl, and S in the fuel has

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been found to correlate linearly with fine particle emissions.[6] However, the release fraction of alkali metals, from the fuel bed into the fine particle fraction, is combustion unit and fuel specific and is affected by the fuel bed temperature and the fuel ash chemical composition.[8,25,26] For the latter, several factors influencing alkali metal release have been identified. It has been reported, for example, that addition of Cl leads to increased particle emissions.[21,27] However, there are also some factors that can inhibit the release of alkali metals from fuel. For example, in S rich fuels, alkali metals tend to form less volatile alkali metal sulfates instead of alkali metal chlorides, which are formed in Cl rich fuels, and Cl is mainly emitted to the gas phase as HCl.[27,28] This phenomenon is well-known to take place in the postcombustion zone of power plants, for example, when peat is added to biomass fuels to prevent the formation of alkali metal chlorides, which cause corrosion in heat exchangers.[7] Silicates also affect the release of alkali metals by forming alkali silicate compounds, which are less volatile and more likely to remain in the bottom ash.[9,16] Thus, also the (K+Na)/Si content of fuel has been reported to affect the fine particle emissions[29] which is due to reduced volatilization of alkali metals.[28]

A few studies have been previously published demonstrating the possible effects of using different raw material pellets in the combustion process of residential heating. These studies have highlighted that raw materials can affect the slagging tendencies,[30] fine particle emissions,[6,21,31] and fine particle properties.[32] However, much more information is needed for understanding the effects of fuel ash properties on particle emissions. In this study, fuel properties and particle emissions from 21 pellet fuels made of different raw materials were investigated. Pellets made of stem wood of different tree species, roundwood, logging residues, bark, peat, straw, and different mixtures were combusted in a 25 kW pellet boiler. Relations between fuel and fine particle characteristics were investigated to gather knowledge on the effects of fuel characteristics on particle formation in residential pellet combustion.

2. EXPERIMENTS

Combustion experiments were performed in a laboratory environment using a 25 kW pellet boiler manufactured by Biotech GmbH (model PZ-RL 25). The boiler operated with a top-feed fuel input and included an integrated burner and boiler. The boiler had separately controlled primary and secondary air inputs and a lambda probe for ensuring sufficient combustion conditions and high efficiency. The boiler was attached to a heat exchanger to cool the system and enable stable operation. The system has been described elsewhere in more detail.[22] Nominal output was used in all of the experiments, and no adjustments were made to combustion behavior between experiments with different fuels. The boiler has been designed for pellet fuels that contain less than 0.5% of ash.

Experiments were carried out with altogether 21 different pellet fuels (Table 1). The used raw material included stem wood, bark, peat, straw, logging residues, and different mixtures of the aforementioned fuels. Fuels were divided into four groups: (1) wood fuels containing wood and/or bark material and later indicated as "W" (woody biomass, stem wood, bark; cases W1 to W11); (2) fuels containing only peat, "P"(cases P1 and P2); (3) fuels containing mixtures of woody biomass and peat "WP" (cases WP1 to WP5); (4) fuels containing straw "S" (cases S1 and S2) and fuels containing a mixture of wood and reed canary grass "WG" (case WG1). Furthermore, the Si/K ratio was used to improve the interpretation of the results. This ratio varies from one fuel type to another, and it is highest with fuels containing peat and rather high with fuels containing straw. The ratio is lowest with fuels containing only stem wood, and it increases if there are some contaminants such as soil in the fuel, while further increase is seen when peat is mixed with woody biomass fuels. The ratio of Si/K varied between 0.03 and 0.6 in wood fuels, 8.2 and 30.6 in peat fuels, 0.9 and 1.8 in wood-peat fuels, and 0.9 and 2.7 in straw and wood-grass fuels (Table 2).

Table 1. Fuel Moisture Content, Ash Content, Net Heating Value, and Ash Fusibility[a]

fuel	abbreviation	moisture, m-%	ash content (%), 550 °C	NHV, MJ/kg	ash fusibility, deformation (DT/A)
woody biomass 1	W1	7.5	0.2	18.91	1450
woody biomass 2	W2	7.7	0.5	18.83	1210
woody biomass 3	W3	9.7	1.3	19.11	1410
woody biomass 4	W4	10.6	2.2	19.48	>1450
woody biomass 5	W5	10.7	0.7	18.72	1230
woody biomass 6	W6	7.3	0.2	19.25	>1450
woody biomass 7	W7	9.3	2.3	19.55	1170
woody biomass 8	W8	10.7	0.7	19.38	1400
woody biomass 9	W9	4.2	0.3	18.97	>1450
woody biomass 10	W10	4.1	0.5	18.95	1410
woody biomass 11	W11	5.9	0.3	19.15	1440
peat 1	P1	18.8	3.2	19.17	1150
peat 2	P2	12.7	1.5	19.63	1170
wood-peat 1	WP1	10.6	0.9	19.12	1160
wood-peat 2	WP2	12.8	1.8	19.45	1220
wood-peat 3	WP3	11.3	2.0	19.43	1260
wood-peat 4	WP4	10.6	1.4	18.94	1160
wood-peat 5	WP5	7.8	0.2	19.23	1330
straw 1	S1	5.4	4.7	17.88	870
straw 2	S2	5.9	5.3	17.69	950
wood-grass 1	WG1	9.9	1.4	18.63	1170

[a] The ash content is the mass percentage of dry fuel, and the moisture content is the mass percentage of wet fuel. NHV, net heating value. The following analysis methods were used: ISO 540:1995 for ash fusibility,[33] CEN/TS 14775 for ash content,[34] and CEN/TS 14918 for heating value.[35]

Fuel properties have been presented in Tables 1 and 2. There was significant variation in fuel properties. Ash content of the fuel varied between 0.2% (W1, W6, WP5) and 5.3% (S2). Generally, woody raw materials had low ash contents, below 0.5%, and straw pellet had the highest ash contents (Table 1). Ash deformation temperatures were the lowest in straw pellets, peat pellets and WG1. Furthermore, the mixtures of peat and woody raw material had lower ash fusibility temperatures than pure woody biomass pellets.

Flue gases were directed to a 3 m high stack (Figure 1) after the boiler, which was an insulated steel pipe with an inside diameter of 180 mm. After the stack, flue gases were directed outside through a hood using a flue gas fan. There was a space between the hood and the stack to ensure a natural draft in the stack and in the boiler. A portion of the flue gases was taken from the stack to a dilution tunnel through a heated (140 °C) and insulated 12 mm diameter sample line. Dilution

Table 2. Fuel Chemical Composition[a]

fuel	Al	Ca	Cl	Fe	K	Na	P	S	Si	Zn	C %	H %	N %
W1	25.3	633	70	66	420	-	60	<200	140	7.04	51.2	6.4	<0.1
W2	71.1	1140	70	370	720	37	130	<200	430	14.6	51.2	6.4	<0.1
W3	224	3060	110	240	1500	100	300	200	690	21.4	52.1	6.3	0.17
W4	31	5040	140	220	2200	130	470	300	760	31.4	53.0	5.9	0.38
W5	18.4	1470	80	210	1000	44	120	<200	350	18.4	50.8	6.4	<0.1
W6	7.82	728	100	33	470	45	49	<200	99	11.4	51.8	6.3	0.11
W7	194	1910	130	270	2400	62	510	400	1300	27.6	52.0	6.0	0.58
W8	301^{+}	6040^{+}	40	120	1100	24	270	<200	210	67.7*	51.6	6.2	0.25
W9	19.7^{+}	558^{+}	20	36	710	24	130	<200	<100	45.9*	50.5	6.2	0.14
W10	1.07^{+}	1040^{+}	20	89	1200	20	210	200	<100	29*	50.5	6.3	0.23
W11	55.4^{+}	589^{+}	20	79	680	30	120	<200	150	17.3*	50.9	6.2	0.12
P1	923	2240	200	3600	121	-	400	1200	3700	5.2	52.1	5.9	1.12
P2	738	1810	210	2900	280	150	280	800	2300	3.39	53.3	6.2	0.71
WP1	338	1400	140	1200	520	100	180	500	950	9.17	52.0	6.3	0.40
WP2	534	3930	180	1200	1400	170	400	500	1300	21.1	53.1	6.0	0.56
WP3	523	4050	150	840	1700	220	430	400	200	22.8	52.9	6.0	0.43
WP4	304	1860	180	1100	1000	97	210	500	1200	17.4	51.8	6.3	0.41
WP5	42.6	765	60	133	430	<25	56	<200	81	8.83	51.4	6.5	0.13
S1	527^{+}	3780^{+}	1600	520	8600	130	1500	1200	7300	652*	47.7	6.0	0.71
S2	55.4^{+}	589^{+}	1100	270	6000	180	1200	1100	10400	17.3*	46.9	5.9	1.03
WG1	36.5	893	150	180	770	50	190	200	2100	12	50.3	6.3	0.28

[a] The elemental analyses are presented as mg kg^{-1} of dry fuel, where other units are not indicated. The following fuel analysis methods were applied: S (ASTM D 4239);[36] Cl (CEN/TS 15289);[37] C, H, N (CEN/TS 15104);[38] Na, K, Fe, P, Si (CEN/TS 15290:2006 A).[39] Zn, HNO$_3$ dissolution in microwave oven (EPA 3051)[40] and inductively coupled mass spectrometry ICP-MS or HF-HNO$_3$ dissolution with ICP-MS (*); Al, Ca, HNO$_3$ dissolution in microwave oven (EPA 3051) and inductively coupled atomic emission spectrometry (ICP-AES) or HF-HNO$_3$ dissolution with ICP-MS from ashed sample (+). Sample was reduced to ash in 520 °C for 12 h.

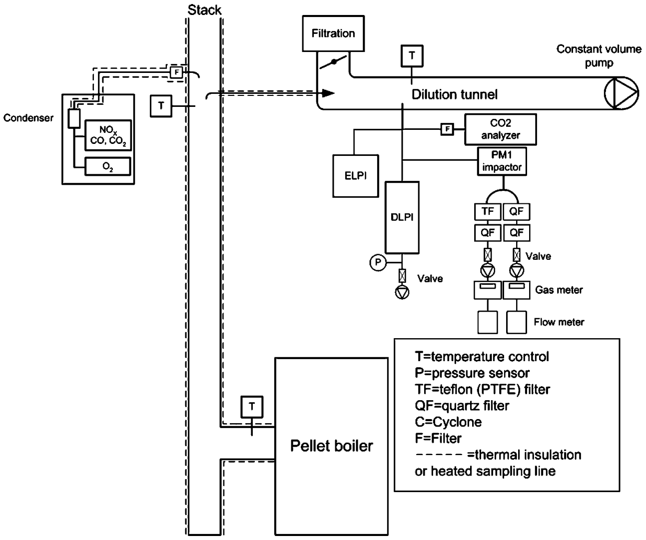

Figure 1. Schematic drawing of the experimental setup.

air in the tunnel was taken from the laboratory air and was filtered to remove nitrogen oxides, hydrocarbons, and particles. The dilution tunnel is 8.5 m long with a 300 mm diameter and has been built according to the standard ISO 8178-1.[41] The volume flow in the dilution tunnel was approximately 650 m^3/h during the experiments. The dilution system has been used previously in many different emissions studies of residential wood combustion.[6,42−44] Flue gas temperatures were measured with K-type thermocouples at the points where the flue gas entered the stack, in the stack where the sample is drawn to the dilution tunnel approximately 3 m after entering the stack, and in the dilution tunnel where the sample was taken (Figure 1).

Dilution ratios (DR) were calculated by using CO$_2$ concentration in the undiluted flue gas and in the diluted flue gas using an equation described by Sippula et al.[45] Particle concentrations were dilution corrected by multiplying results with the DR and calculated as dry flue gas. All of the emission results were calculated in relation to fuel energy input to the burning process.[46]

Table 3. Gaseous Emissions, Dilution Ratios, Sample Temperatures, Flue Gas Temperatures, and Air-to-Fuel Ratio[a]

fuel	λ	flue gas T, °C	sample gas T, °C	DR	CO	OGC	NO_X	SO_2	HCl
W1	1.9	145 ± 2.07	33.3 ± 1.84	128 ± 6.30	107 ± 108	0.76 ± 0.54	60.7 ± 1.79	0.00 ± 0.06	0.19 ± 0.13
W2	1.8	155 ± 3.49	27.8 ± 0.77	164 ± 14.8	206 ± 161	1.52 ± 1.49	81.9 ± 3.07	0.15 ± 0.53	0.27 ± 0.14
W3	2.0	159 ± 4.52	27.3 ± 0.78	158 ± 10.4	106 ± 37.2	1.04 ± 0.37	128 ± 4.96	0.05 ± 0.18	0.26 ± 0.13
W4	2.0	150 ± 1.34	24.6 ± 1.10	143 ± 6.16	127 ± 58.3	0.83 ± 0.26	134 ± 4.68	2.21 ± 2.75	0.08 ± 0.09
W5	2.0	155 ± 1.88	27.4 ± 0.70	163 ± 13.7	94.8 ± 42.3	1.11 ± 0.49	79.7 ± 2.44	-	-
W6	1.9	153 ± 2.90	25.5 ± 0.87	138 ± 6.10	185 ± 170	1.16 ± 1.34	50.2 ± 1.39	7.54 ± 0.56	0.08 ± 0.09
W7	2.1	151 ± 2.93	27.1 ± 0.68	128 ± 8.04	236 ± 113	3.38 ± 1.88	168 ± 7.98	13.3 ± 1.49	0.24 ± 0.29
W8	2.2	139 ± 2.90	27.2 ± 0.97	125 ± 21.2	316 ± 138	4.66 ± 2.74	112 ± 4.25	4.80 ± 5.55	0.02 ± 0.02
W9	2.0	138 ± 2.68	18.8 ± 1.16	109 ± 9.23	279 ± 377	3.33 ± 7.41	80.2 ± 3.67	1.68 ± 0.42	0.13 ± 0.09
W10	1.9	131 ± 2.84	22.6 ± 0.78	106 ± 14.0	455 ± 408	4.21 ± 7.46	126 ± 6.72	2.35 ± 0.50	0.27 ± 0.19
W11	1.9	137 ± 1.77	22.2 ± 0.83	106 ± 5.43	121 ± 126	0.90 ± 1.39	71.0 ± 2.01	2.42 ± 0.31	0.10 ± 0.08
P1	2.9	134 ± 2.97	29.3 ± 0.47	135 ± 30.6	398 ± 324	6.58 ± 6.04	438 ± 32.5	100 ± 13.1	0.60 ± 2.00
P2	1.9	146 ± 2.97	26.1 ± 1.44	139 ± 2.31	8.76 ± 30.5	0.53 ± 0.18	249 ± 17.4	97.7 ± 6.16	1.93 ± 0.95
WP1	1.9	161 ± 1.76	28.6 ± 1.20	163 ± 13.3	13.2 ± 21.8	0.41 ± 0.13	155 ± 5.35	-	-
WP2	1.9	159 ± 4.02	27.5 ± 0.80	159 ± 8.90	24.0 ± 9.74	0.46 ± 0.09	260 ± 9.05	-	-
WP3	1.9	157 ± 2.40	27.5 ± 0.88	162 ± 11.0	43.6 ± 18.7	0.50 ± 0.10	156 ± 6.61	22.6 ± 0.87	0.17 ± 0.06
WP4	1.9	157 ± 2.01	27.4 ± 0.78	164 ± 3.45	38.1 ± 18.2	0.64 ± 0.25	149 ± 4.01	32.9 ± 1.03	0.20 ± 0.07
WP5	1.8	145 ± 2.92	25.6 ± 1.04	133 ± 2.43	181 ± 175	1.32 ± 1.93	60.9 ± 2.13	9.05 ± 2.86	0.27 ± 0.13
S1	2.4	144 ± 23.0	29.0 ± 0.93	187 ± 41.8	728 ± 1480	-	292 ± 43.3	37.6 ± 10.4	9.87 ± 3.41
S2	2.2	148 ± 26.3	31.7 ± 0.75	185 ± 20.8	311 ± 256	-	305 ± 47.8	41.4 ± 3.31	12.46 ± 3.99
WG1	2.4	142 ± 9.29	24.1 ± 1.49	140 ± 25.5	1250 ± 2030	17.2 ± 134	122 ± 54.0	21.1 ± 8.04	0.11 ± 1.28

[a] Emissions of CO, OGC, NO_X, SO_2, and HCl are presented as average emissions factors (mg MJ^{-1}).

Combustion Procedure and Sampling Times. The boiler was turned on approximately three hours before the start of the experiment to ensure stability during the experiment. Each measurement lasted 6–7 h, and during this time three 1.5–2 h filter samples were collected. Collection of particles with Dekati Low Pressure Impactor (DLPI, Dekati Ltd.) and online measurement devices were sampling throughout the whole experiment. Averaged values for the experiment period were taken from the continuous measurements and are presented later. In general, the relatively short experiment time compared to real-life usage enabled sufficient combustion, including with ash-rich fuels. However, the experiments with S1 and S2 needed to be modified due to severe ash melting problems: each filter collection lasted only 1 h and between the first and the second filter collections a manual grate-cleaning procedure was implemented to remove partly melted ash from the grate and to provide satisfactory stability for combustion through the experiment.

Gas Measurements. Gas emissions were measured in the stack with two measurement devices: First, an ABB Hartman & Braun gas analyzer system (ABB Cemas Gas Analyzing Rack, ABB Automation GmbH), which continuously measures O_2, NO_X, CO, and CO_2 and also includes a flame ionization detector (FID) for organic gaseous carbon (OGC) measurement, and second, a Fourier Transform Infrared gas analyzer (FTIR, Gasmet Technologies Ltd.). Furthermore, a CO_2 analyzer (ABB AO2040, Uras 14, ABB Automation GmbH) was used for continuous measurement of CO_2 concentration in the diluted sample gas to calculate the DR in the diluted sample.

Particle Measurements. Particle measurements were done for the diluted sample in the dilution tunnel, where DR varied between 106 (W11) and 187 (S2) (Table 3). Particle measurements included number-size distribution with an Electrical Low Pressure Impactor (ELPI, Dekati Ltd.), mass-size distributions with a DLPI and PM_1 filter collections. The ELPI was operated with a flow rate of 10 lpm and with sintered impaction plates. A filter stage was applied in ELPI for tests of P2, W4, WP5, W6–W8, and S1. The mass-size distribution measurement with a DLPI was carried out with aluminum impaction plates, which were greased with toluene–Apiezon-L (M and I Materials Ltd.) solution to prevent particle bouncing. PM_1 filter collection included two parallel systems, which both included precutoff cascade impactors (Dekati Ltd.) with a 1 μm cutoff diameter. First, a PM_1 sample was collected on a polytetrafluoroethylene (PTFE, PALL Life Sciences; type: Teflo P/N R2PJO47) filter and second, a set of one PTFE filter and three quartz filters (PALLFLEX Membrae Filter; type: Tissuequartz 2500QAT-UP) were used with organic and elemental carbon contents from these filters analyzed.[22] All of the filters were placed on a 47 mm stainless steel filter holder (Gelman Sciences, model 2220). Gravimetric analyses were performed with a microbalance (Mettler-Toledo MT5) prior to and after the collection in a room with stable conditions (RH 40%, 20 °C) where they were kept at least 24 h prior to weighing.

Particle Analyses. Organic (OC), elemental (EC), and carbonate (CO_3) carbon analyses were performed for the quartz filter samples with a thermal-optical method[47] using a Carbon Aerosol Analyzer (Sun Laboratories Inc.) according to the National Institute for Occupational Health NIOSH 5040 procedure.[48] A detailed description of the OC/EC collection and analyses used in this study has been presented elsewhere.[6,45]

The elemental analyses (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Th,, Ti, Tl, U, V, and Zn) were conducted from three replicate filter samples for each fuel with ICP-MS (hydrofluoric acid and nitric acid dissolution), and anions (Br, Cl, F, SO_4, NO_3, PO_4) were analyzed with ion chromatography (IC, water dissolution).

3. RESULTS

The combustion process stayed relatively stable during the experiments due to the automatic operation of the pellet boiler. Flue gas temperatures, which were measured at the point where flue gases entered the stack, varied from 134 °C (P1) to 161 °C (WP1) (Table 3). In most experiments the standard deviations of the average temperatures were approximately 2–4 °C, but the problems in the combustion of straw pellets increased the variation of flue gas temperatures (Table 3) as well as that of other combustion parameters. The lowest air-to-fuel ratio was in WP5 (1.82) (Table 3) and the highest in P1 (2.63). The average air-to-fuel ratio of all experiments was 2.01. The filter samples for P1 and WG1 were excluded from the data analysis of the last measurement periods, as were the results from the continuous measurement devices, due to significant variation in the process. However, DLPI measurement was done throughout the whole experiment.

Gaseous Emissions. CO and OGC emissions from automated pellet combustion devices are generally low, which is achieved by precise control of the process. However, varying pellet raw materials significantly altered the gaseous emissions that were measured. The lowest CO and OGC emissions were measured for the fuels containing peat (plain or mixed), except in P1 where ash melt on the grate affected the combustion, especially toward the end of the experiment (Table 3). The lowest CO emission factor was measured from P2 (8.8 mg/MJ) and the highest from WG1 (1250 mg/MJ). CO emission factors from most of the fuels were under 200 mg/MJ (Table 3), and elevated CO emission factors were measured from W2, W7−W10 and S1, S2, and WG1. The OGC emissions varied between 0.41 mgC/MJ (WP1) and 17 mgC/MJ (WG1) (OGC was not measured from straw pellets). Generally, the OGC emission factors were under 2 mgC/MJ. Pellets containing peat and straw, which also had higher sulfur content, had notable SO_2 emissions, with the highest emission of 100 mg/MJ (P1). Fuels containing only stem wood and bark had very low SO_2 emissions, being close to the detection limit of the FTIR analyzer (Table 4). HCl emissions were generally low. Only S1 and S2 produced considerable HCl emissions, 9.9 mg/MJ and 12 mg/MJ, respectively. Straw pellets also had the highest fuel Cl concentrations. NO_X emissions were strongly affected by the fuel N content and varied between 50 mg/MJ and 440 mg/MJ from W6 and P1, respectively.

Table 4. Emission Factors of PM_1, Carbon Compounds, Number Emissions, and Mean Particle Sizes[a]

fuel	PM_1	OC	EC	CO_3	N_{Tot}	GMD	MMD
W1	12.4	0.28	0.7	0.74	1.6×10^{13}	68.6	138.9
W2	13.8	0.71	2.54	0.28	6.2×10^{13}	55.3	108.2
W3	28.0	0.56	0.21	0.20	5.8×10^{13}	69.7	156.2
W4	45.8	0	0.21	0.76	4.3×10^{13}	83.6	182.2
W5	20.7	0.26	0.39	1.01	5.3×10^{13}	62.4	131.8
W6	18.3	0	0.33	0	5.1×10^{13}	53.0	104.8
W7	27.5	0.80	0.21	0	5.4×10^{13}	70.8	154.4
W8	19.1	0.60	0.34	0	3.8×10^{13}	69.3	157.4
W9	14.0	1.28	5.63	0	7.7×10^{13}	51.5	119.2
W10	22.8	0.23	4.81	0	6.7×10^{13}	69.5	176.7
W11	9.7	0.82	2.04	0	6.0×10^{13}	51.2	157.5
P1	5.1	0.74	0.06	0.71	1.9×10^{13}	55.9	504.3
P2	2.9	0	0.09	0.45	3.4×10^{13}	43.6	234.3
WP1	5.2	0.21	0.15	0.84	2.4×10^{13}	53.1	154.7
WP2	22.7	0.50	0.17	0.21	4.2×10^{13}	74.0	151.7
WP3	27.7	0.48	0.12	0.78	4.4×10^{13}	77.5	152.9
WP4	11.2	0.11	0.23	0	2.8×10^{13}	65.6	139.7
WP5	10.8	1.06	1.73	0.54	4.5×10^{13}	46.1	112.8
S1	195.5	1.84	1.23	0	9.5×10^{13}	136.5	230.5
S2	125.7	2.20	23.1	0	7.5×10^{13}	127.9	242.7
WG1	23.0	2.07	2.62	0.69	5.8×10^{13}	50.8	126.1

[a] PM_1, EC, OC, CO_3, mg MJ^{-1}; N_{Tot}, # MJ^{-1}; GMD, and MMD, nm. The values from continuous measurements (N_{Tot} and GMD) are average values from the experiment period.

Particle Emissions. *Particle Size Distributions and Number Emissions.* Only unimodal particle number-size distributions were measured. A 6-fold difference was seen between the lowest (1.6×10^{13} #/MJ) and the highest (9.5×10^{13} #/MJ) number emissions, which were from W1 and S1, respectively (Table 4). The lowest particle number emissions were measured from fuels containing peat and/or stem wood, but not bark, which seems to increase the number emissions. However, the largest emissions were measured from straw pellets (S1 and S2). Particle geometric mean diameters (GMD) varied between 43 nm (P2) and 136 nm (S1). Only S1, S2, and W4 had GMD over 80 nm, and particles from fuels containing bark or straw seem to have slightly larger particle size than those from pellets containing only woody biomass or peat. Mass mean diameters (MMD) were calculated from DLPI results, and they varied between 104 nm (W6) and 504 nm (P1) (Table 5). The highest mass concentrations and particle sizes were observed for S1 and S2. All MMDs, excluding those from peat and straw pellet fuels, were below 200 nm. Mass-size distributions, except P1, were generally unimodal, and the particle mass was almost entirely in the fine mode (<1 um). However, in some cases particles were found also outside the fine particle mode in the size range 1−10 μm. Particularly with P1, about 44% of the PM10 mass was observed in the size range 1−10 μm.

Fine Particle Mass Emissions. PM_1 emissions varied considerably between the extremes of 5.1 mg/MJ and 195 mg/MJ from P1 and S1, respectively (Table 4). Generally, fuels containing peat had small PM_1 emissions, and mixing of peat with other raw materials decreased the emissions of PM_1. Fuels containing stem wood also had relatively small PM_1 emissions, while increased K content in the fuels increased the emissions. Straw fuels had clearly the highest PM_1 emissions.

Particle Chemical Composition. PM_1 was mainly composed of ash components (Table 5). The most abundant ash species were potassium (K) and sulfate (SO_4). Other common ash species were Na, Zn, Cl, CO_3, and NO_3. Detectable amounts of PO_4 were found from the samples of S1 and S2. For most of the fuels PM_1 did not contain large amounts of EC or OC, which comprised less than 10% of the total PM_1. Due to variation in the process, there were some exceptions where 20−49% of the PM_1 contained unburned carbon, EC, and OC (Table 4).

Release Fractions of Ash Forming Elements: K, Na, Cl, S, and Zn. The release fractions of ash forming elements, K, Na, S, Zn, and Cl, to PM_1 were calculated based on fuel concentrations and PM_1 concentrations in the samples (Table 6). The release of S and Cl into gas phase components of SO_2 and HCl were also taken into account. The release fractions of K to PM_1 varied between 2.8% and 15.7% from WG1 and S1, respectively, though it was generally between 8% and 12%. The lowest release fractions of K to PM_1 were found for P2, WP1, and WG1 and the highest for W3, WP3, W4, W5, W6, and S1.

Release fractions of Na to PM_1 varied significantly from 0.4% to 13% for W9 and W8, respectively, but were mainly between 5% and 7% (Table 6). Na did not contribute a significant fraction of PM_1. Release fractions of Zn to PM_1 varied more significantly between different fuels. The highest release was 63.8% (P2) and the lowest 4.8% (W11). The release fraction of Zn to PM_1 stayed relatively constant within the different fuel groups, but it seems to decrease with increasing fuel Zn content. However, there were some exceptions, such as W9 and W11, where the release fraction was significantly lower than with other fuels.

The release fraction of S to PM_1 varied significantly in accordance with the fuel properties (Table 6). For pellets containing woody biomass, 20 to 55% of S was found in PM_1 as SO_4 (except W6, 10%). Furthermore, from WP fuels the releases of S to PM_1 decreased and S shifted from PM_1 to the gas phase as SO_2 (Table 3). The release fraction of S to the gas

Table 5. Emission Factors for the Ash-Forming Content and Content of Individual Metals (mg MJ^{-1}) of Emitted PM_1[a]

fuel	Cl	Ca	K	Na	Zn	Fe	NO_3	SO_4	PO_4	other analyzed
W1	<DL	0.33	2.76	0.11	0.14	0.21	0.42	2.22	<DL	0.68
W2	0.88	0.33	3.49	0.24	0.26	<DL	<DL	3.37	<DL	0.14
W3	1.13	0.26	8.27	0.62	0.46	<DL	<DL	11.49	<DL	0.30
W4	1.30	<DL	12.9	0.65	0.62	0.18	0.29	17.6	<DL	0.29
W5	0.66	0.25	6.49	0.23	0.38	0.14	<DL	6.98	<DL	0.19
W6	2.58	<DL	2.72	1.69	0.15	0.10	<DL	2.36	<DL	0.15
W7	2.59	0.16	8.19	0.21	0.89	<DL	<DL	8.75	<DL	0.19
W8	1.03	0.29	5.04	0.16	0.34	<DL	<DL	6.06	<DL	0.15
W9	0.71	<DL	2.77	0.005	0.20	<DL	0.18	2.66	<DL	0.02
W10	1.42	<DL	5.11	<DL	0.24	<DL	0.17	6.46	<DL	0.06
W11	0.76	<DL	2.45	0.02	0.04	<DL	0.15	2.63	<DL	0.02
P1	<DL	0.41	0.58	0.32	0.14	0.24	<DL	1.32	<DL	0.33
P2	<DL	<DL	0.48	0.48	0.11	0.37	<DL	1.04	<DL	0.26
WP1	0.61	0.24	1.60	0.23	0.22	0.10	<DL	1.07	<DL	0.12
WP2	3.06	0.25	6.81	0.83	0.46	0.15	<DL	6.90	<DL	0.33
WP3	2.33	0.17	8.84	0.84	0.53	0.09	<DL	10.3	<DL	0.18
WP4	1.84	0.19	3.47	0.28	0.41	0.09	<DL	2.29	<DL	0.14
WP5	0.68	<DL	1.88	0.10	0.13	0.14	<DL	1.63	<DL	0.15
S1	43.9	<DL	71.34	0.35	0.72	0.11	<DL	14.4	10.1	0.17
S2	16.8	<DL	27.41	0.61	0.41	0.03	<DL	4.32	13.8	0.61
WG1	0.30	<DL	1.17	0.14	0.24	0.25	<DL	0.45	<DL	0.21

[a] "Other analyzed" is the sum of other chemical components that were analyzed but are not presented. <DL, under detection limit.

Table 6. Release Fractions of K, Na, Cl, S, and P from Fuel to Flue Gas as PM_1 and Gas Compounds[a]

	PM_1 (%)						stack gas (%)	
fuel	K	Cl	S	Na	P	Zn	S	Cl
W1	12.4	-	-	-	-	38.3	-	5.3
W2	9.1	23.6	-	12.1	-	33.8	-	6.9
W3	10.5	19.7	36.7	11.9	-	41.2	0.25	4.4
W4	13.2	18.1	38.0	9.8	-	38.5	7.2	1.1
W5	12.2	15.5	-	9.9	-	38.7	-	-
W6	11.1	49.7	-	(72.2)	-	26.0	-	1.6
W7	6.7	39.0	14.3	6.5	-	25.7	32.6	3.5
W8	8.8	49.6	-	13.0	-	23.8	-	0.97
W9	7.4	67.1	-	0.40	-	8.6	-	11.7
W10	8.1	134	20.4	-	-	15.9	11.2	25.0
W11	6.8	72	-	1.4	-	4.8	-	8.9
P1	9.2	-	0.70	-	-	51.7	80.2	5.6
P2	3.3	-	0.85	6.2	-	63.8	(120)	17.5
WP1	5.9	8.4	1.36	4.3	-	46.4	-	-
WP2	9.5	33.1	9.0	9.4	-	42.6	-	-
WP3	10.1	30.2	16.7	7.4	-	45.1	55.0	2.1
WP4	6.6	19.4	2.9	5.4	-	44.7	62.3	2.0
WP5	8.4	21.9	-	-	-	27.9	-	8.4
S1	15.7	52.0	7.6	5.1	3.9	20.9	28.0	10.7
S2	8.7	19.9	2.3	6.4	6.6	11.9	33.3	19.5
WG1	2.8	3.7	1.4	5.2	-	36.7	98.4	1.4

[a] For some fuels and elements, the release fraction could not be measured because of the fuel concentration or/and PM_1 concentration were under the detection limit.

phase as SO_2 varied between 0.25% (W3) and 98.4% (WG1) (Table 6). Most of the PM_1 samples contained Cl (Table 3). For P1 and P2, no Cl was detected from the PM_1. The release fraction of Cl to the gas phase varied from 0.97% (W8) to 25% (W10).

4. DISCUSSION

The pellet boiler in this study was designed for low ash content fuels, but short experiment periods enabled stable processes. However, some variation in emissions was seen in high ash content and low ash melting fuels. Elevated CO and OGC emissions factors, for example, indicated such problems in WG1, P1, S1, and S2. In most of the experiments, PM_1 emissions were mainly comprised of particle ash, and emissions from incomplete combustion were low. This is typical for well-controlled pellet boilers and burners.[6,21,29] Typical ash species in PM_1 have been previously identified as sulfates, chlorides, and carbonates of alkali metals (K and Na) and zinc oxide (ZnO).[6,49]

Fuels Containing Woody Biomass. Altogether 14 types of wood, bark, and wood-bark mixtures were used in the experiments. Such fuels have a Si/K ratio smaller than 0.60 and typically low ash and Si content, and high ash melting temperatures, indicating that slagging is unlikely to happen in small-scale appliances. Gaseous emissions, CO, OGC, SO_2, HCl, and NO_X, were generally low or around the average of other results in this study. However, there were some exceptions, such as W8 and W10, from which CO and OGC emissions were slightly increased.

Fuels containing wood and/or bark were S and Cl poor, and (K+Na)/(Cl+2S) molar ratios varied from 2.2 to 34. The ratios above one are known to indicate low emissions of SO_2 and HCl.[50,51] Thus, the fuel S is mainly bound as SO_4 in PM_1 (Table 6). However W7, for example, produced SO_2 emissions of 13.3 mg/MJ, which was higher than from other wood/bark fuels but lower than from peat or straw fuels (Table 3). This can be explained with the lowest (K+Na)/(Cl+2S) molar ratio within this group.

The fuels with the largest amounts of potassium within this group, W4 and W7, produced the largest PM_1 emissions. K and SO_4 were the most abundant components in the samples, showing that the major compound in PM_1 was K_2SO_4. The release fractions of K and Na to PM_1 were relatively high, which was probably due to low fuel Si contents[29] and low S content.[52] Furthermore, clear differences in PM_1 emissions of two fuels (W4 and W7) with similar amounts of alkali metals were probably due to different Si contents in the fuels. The results are in agreement with earlier studies,[6,29,31,53] showing that the K content of fuel plays an important role in the formation of fine particles. Furthermore, similar to earlier studies,[9,25] the results here indicate that Si in fuel decreases alkali metal release in small-scale pellet combustion.

Peat Fuels. The chemical composition of the peat fuels differed significantly from the biomass fuels, but also the two peat pellets had significant differences in their chemical compositions (Tables 1 and 2). Peat fuels contained more Si, S, and Fe but less alkali metals than the woody biomass fuels. Due to this, the fine particle emissions and K-release fraction to fine particle were low with peat fuels. On the other hand, due to the low (K+Na)/(Cl+2S) ratio of the fuel, there were elevated SO_2 and HCl emissions. SO_2 emissions from peat fuels were about 2-fold those of S1 and S2, even though the sulfur contents of the fuels were roughly the same.

CO and OGC emissions from P2 were small, but the emissions from P1 were clearly affected by the ash melt on the grate which interrupted the combustion toward the end of the experiment. Despite this, the emissions of OC and EC in PM_1 were low for both peat fuels. Previous studies have reported larger particle emissions[54] and emissions of organic gaseous compounds[55] for peat than wood fuels. However, these results are most likely connected to insufficient combustion conditions for peat fuels rather than to peat pellet qualities in general.

Generally, the use of pure peat fuels is a little troublesome in residential pellet appliances, which are designed for low ash fuel qualities, due to the low ash melting temperature and relatively high ash content (Tables 1 and 2). In combustion appliances that are designed for high ash content fuels, it should be possible to use peat pellets without problems. However, SO_2 and HCl emissions from peat pellets are higher compared to woody biomass pellets and are difficult to avoid in small-scale systems. Therefore blending of peat with woody biomass is an attractive option.

Mixtures of Woody Biomass and Peat. Five different mixtures of woody biomass and peat were studied. The CO and OGC emissions were generally low and lower than those measured from woody biomass fuels alone (Table 3). These results indicate that peat has a decreasing effect on CO and OGC emissions when it is mixed with woody biomass. The SO_2 and HCl emissions were higher than with wood pellets, as can be expected from the lower (K+Na)/(Cl+2S) ratios, compared to woody pellets. A very low PM_1 emission (5.2 mg/MJ) factor was measured for WP1 (Table 4), which was surprising since the sum of K+Na+Cl in the fuel, for example, was larger than that of W1 (PM_1 emission 12.4 mg/MJ). Thus the release of K in WP1 was relatively low (6%) and clearly indicates that the addition of peat to woody biomass decreases PM_1 emissions (Table 6). This can be due to two reasons. First, the low fuel Cl/S ratio prefers formation of alkali sulfates instead of chlorides which may decrease volatilization of alkali metals from the fuel bed.[28] Second, the high fuel Si content increases formation of alkali metal silicates and consequently prevents release of alkali metals into fine particle fractions[16,56]

Fuels with Agricultural Biomass. Straw and wood-grass (S1, S2, and WG1) had high ash contents and significantly different fuel ash characteristics compared to the other fuels studied. Especially S1 and S2, but also WG1, had low ash melting temperatures causing formation of ash melt on the grate, which disturbed the combustion process by interfering with the air input at the grate, as well as high concentrations of Si, P, K, Cl, and S (Tables 1 and 2).

Because of the slightly modified experiment procedure with straw fuels, it was possible to keep incomplete combustion at a tolerable level, and the particle emissions were mainly composed of ash species. However, emissions of CO were slightly higher from WG1 and S1, compared to woody biomass fuels (Table 3). The (K+Na)/(Cl+2S) ratio was roughly the same as in WP fuels. The release fraction of S to gas from S1 and S2 was clearly lower than from peat fuels, and the release fraction of Cl to the gas phase was similar to that of peat fuels (Table 6). Even though the contents of S and Cl in the fuel were high, the low release fractions to the gas phase resulted in only moderate formation of SO_2 and HCl emissions. On the contrary, PM_1 emissions from S1 and S2 were 195 mg/MJ and 126 mg/MJ, respectively, and the GMD was about double that of other fuels. Similarly, the PM_1 contained a significant amount of K, most likely in the form of KCl salts, as can be seen from the small content of SO_4 and high content of Cl in PM_1. In addition, PO_4 was found in PM_1 from straw fuels, which are most likely present as K-phosphates.[21] The release of K was 16% from S1, which was the highest in this study (Table 6). Together with high K fuel content, this resulted in very high K emissions. The release fractions of Cl to PM_1 were 20−52%. Generally, straw pellets are not recommended for use in residential combustion appliances[57] because of their high ash, N, Cl, and K content, which cause problems in emissions, deposit formation, and corrosion. These conclusions are well supported by the results of this study.

Correlations. Linear correlations between fuels and emission characteristics were analyzed from the results. The goal was to investigate if some fuel characteristics could explain the formation of PM_1 and gaseous emissions. Due to the very different fuel characteristics of S1 and S2, the correlations without these two fuels were studied as well.

For wood fuels, fuel ash content has previously been found to correlate with PM_1 emissions,[6] but in this study, only a weak correlation was found between fuel ash and PM_1 emission factors ($R^2 = 0.63$); if S1 and S2 are excluded from the data, the correlation was nonexistent. However, the sum of K, Na, and Cl in the fuel, were clearly found to correlate with the PM_1 emission factors (Figure 3), giving $R^2 = 0.98$ with all experimental data points, and $R^2 = 0.72$ with S1 and S2 excluded from the inspection of the results. In addition, simply the fuel's K content was found to correlate with the PM_1 emissions factor ($R^2 = 0.98$, $R^2 = 0.75$ without straw pellets) (Figure 2). Cl, which is also known to be important in PM_1 formation in combustion of biomass,[27,28] correlated with the PM_1 emission factors ($R^2 = 0.93$), but there was no correlation with the S1 and S2 excluded from the analysis. Fuel (K+Na)*2Cl/S (molar ratio) correlated with the sum of K and Na in PM_1 ($R^2 = 0.95$ and $R^2 = 0.71$ without straw pellets) (Figure 5). Good correlations between the values may indicate that the fuel Cl/S ratio affects the alkali metal release which agrees with earlier findings.[27,28] However, some of the high-sulfur content fuels, as peat, contained also silicates which also affect the alkali metal release. Therefore, differences between alkali metal release fractions are most likely combined effects of both fuel Cl/S ratio and Si content of the fuels. NO_X emissions clearly correlated with fuel N concentrations, showing that NO_X emissions are formed mainly from the fuel N, while thermal-NO_X formation does not influence the emissions[7] (Figure 4).

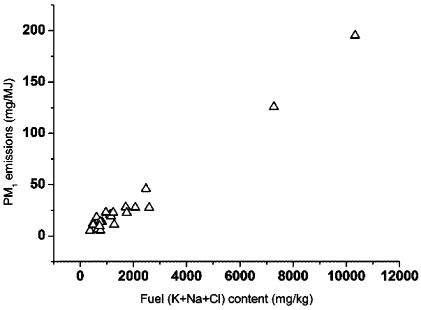

Figure 2. Correlation between the sum of K, Na, and Cl in the fuel and PM_1 emissions.

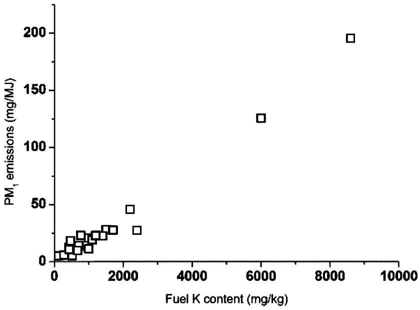

Figure 3. Correlation between fuel K content and PM_1 emissions.

Zinc was the most abundant metal found in the fine particle emissions and is interesting due to its adverse health effects.[58] In theory zinc should mainly be released fully from the fuel as elemental Zn vapor and enrich in fine particles. However, the observed zinc release fractions showed significant variation and values substantially below 100%, but factors affecting the release could not be identified from this data set. Thus, this issue on the zinc mass balance would require further studies.

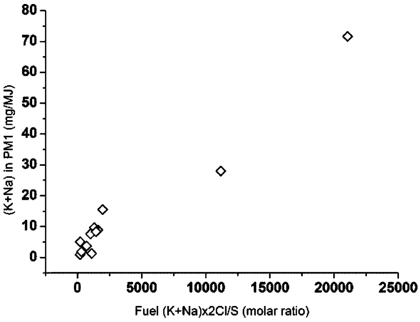

Figure 4. Correlation between fuel (K+Na)*2Cl/S molar ratio and K+Na in PM_1.

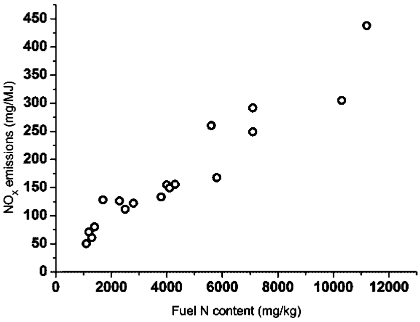

Figure 5. Correlation between fuel N content and NO_X emissions.

5. CONCLUSIONS

This study shows a significant effect of biomass pellet fuel properties on fine particle and gaseous emissions from residential scale boilers. PM_1 emissions varied from 5.1 mg/MJ (peat) to 196 mg/MJ (straw). The particle emissions were mainly composed of K and SO_4; straw pellets also contained noticeable amounts of Cl and PO_4. Since an automated pellet boiler was used, emissions of incomplete combustion were generally low, though elevated emissions of incomplete combustion were measured in wood-grass and some woody biomass pellets (WG1, W8, W9, and W10).

PM_1 and gaseous emissions were generally low for pellets containing mainly stem wood. On the contrary, bark, for example, which contains a lot of K, can contribute to increased PM_1 emissions. However, it may be possible to improve the use of high alkali content fuels by mixing other raw material such as peat, which in this study resulted in a lower release fraction of K to PM_1 and, thus, lower PM_1 emissions. The study shows that there are correlations between certain fuel properties and emission characteristics, which could be used for predicting the emissions from novel pellet raw materials. However, it must be noted that the behavior of different fuels can vary according to the studied combustion appliance type and combustion conditions at issue.

The fuel molar ratio (K+Na)*(2Cl/S) was found to correlate with the release fractions of K+Na to PM_1, which was the major factor found influencing PM_1 emissions for most of the fuels. However, the observed differences in alkali metal release fractions can be also combined effects of sulfur and silicates, as there is a weak correlation between these elements in the fuels. In addition, the amount of alkali metals in particulate fraction from different fuels may be predicted based on fuel alkali metal content, fuel K, and fuel K+Na+Cl; both factors correlated with PM_1 emissions. These findings highlight the importance of alkali metals with respect to PM_1 emissions. Furthermore, peat decreased CO and OGC emissions when mixed with woody biomass fuels but resulted in higher NO_X, SO_2, and HCl emissions. The fuel (K+Na)/(Cl+2S) molar ratio was found to give a good estimation of SO_2 and HCl emission formation. In addition, fuel N content was found to correlate well with the NO_X emissions.

The use of alkali binding additives could give a possibility to use a wider range of biomass pellet raw materials and achieve low PM_1 emissions. However, there is not yet enough information available about the usage of peat as an additive for particle emission control; it should be studied more carefully. The present legislation gives a possibility to use up to 20% of additives in pellet fuels, and, according to our findings, a 20% addition of peat to bark could decrease the otherwise high PM_1 emissions. Agricultural fuels, such as straw pellets, seem to be difficult to use in a residential scale due to high emissions and ash-related problems.

Pellet combustion is a promising means of energy production in residential combustion appliances, replacing fossil fuel. A mixture of peat with woody biomass fuels could lower the emissions of PM_1, CO, and OGC compared to woody biomass fuels. Automated operation generally ensures low emissions of particle and gaseous components from incomplete combustion with suitable fuel types. However, if new fuel raw materials are introduced, the emissions need to be carefully estimated to prevent an increase in particle emissions, which can affect the local air quality and cause adverse effects on human health.

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Notes

The authors declare no competing financial interest.

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Paper IV

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Comparison of emissions and toxicological properties of fine particles from wood and oil boilers in small (20–25 kW) and medium (5–10 MW) scale

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HIGHLIGHTS

- The use of fossil fuels versus wood fuels was compared.
- Gaseous and particle emissions and the cytotoxicity of PM_1 were examined.
- HFO combustion PM_1 was found to evoke the highest toxicity responses.
- Toxicity of emissions should be considered when authorities regulate emission limits.

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ABSTRACT

The aim of this study was to compare four alternatives for providing decentralized energy production in small communities in terms of their flue gas emissions and toxicological properties of the emissions. In this study, two different size classes of boilers were examined and the use of fossil fuel oils was compared against wood fuels. The lowest PM_1 emission, 0.1 mg MJ^{-1}, was observed from small-scale light fuel oil combustion. In medium-scale wood combustion, PM_1 emission values from a grate fired wood combustion boiler (10 MW) without particulate filtration were the highest (264 mg MJ^{-1}) but were substantially reduced down to 0.6 mg MJ^{-1} due to the usage of an electrostatic precipitator (ESP). The wood combustion particles were mainly formed of potassium salts. In light fuel oil combustion, one of the main components in the particles was sulphate whereas in heavy fuel oil combustion also significant amounts of V and Ni were emitted. Pellet combustion produced the lowest PAH emissions. Overall, oil combustion produced higher amount of PAHs than wood combustion. This was indicated also as a higher cytotoxicity of the oil combustion samples when compared to those from wood combustion in the corresponding scale of boilers. However, when calculated on an equal mass basis, the particles collected after ESP were even more cytotoxic which can be explained by the altered chemical characteristics of the emissions in the ESP. Due to the variation in the emissions and in the toxicity of the emissions, we propose that in the long term, not only the emission levels but also the toxicity of the emissions should be taken into account in the regulations of the emission limits of the combustion plants.

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1. Introduction

Fossil fuel combustion is considered to be problematic because it is a significant source of greenhouse gas emissions into the atmosphere and because of the limited resources of the fossil fuels. An increase in biomass use as an energy source holds the potential

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to reduce these emissions, since biomass combustion is currently not considered to affect the carbon dioxide (CO_2) balance in the atmosphere. In addition, biomass combustion can have political support in countries where there are no fossil fuel deposits but are endowed with substantial biomass resources (Obernberger and Thek, 2010). However, one of the major problems with the biomass combustion is its tendency to emit an abundance of fine particles. For example in Finland, it has been estimated that 25% of all fine particle (aerodynamic diameter <2.5 μm) emissions originate from domestic wood combustion (Karvosenoja et al., 2008). In addition, small and medium scale district heating units may generate substantial amounts of PM_1 (particles <1 μm in aerodynamic diameter) emissions if they are not equipped with efficient filtration systems (Sippula et al., 2009a). Different filtration techniques such as electrostatic precipitators (ESPs), flue gas scrubbers and fabric filters reduce the emissions from biomass combustion to a moderate or even to a low level.

In addition to particulate emissions, both biomass and fossil fuel combustion can release varying amounts of nitrogen oxides (NO_x) and sulphur dioxide (SO_2) emissions into the atmosphere. SO_2 emissions are generally related to the fossil fuel combustion but they can be significant also in the combustion of many field biomasses due to the high sulphur content of that kind of fuel (Tissari et al., 2008). NO_x and SO_2 emissions induce secondary particle formation and therefore they can have significant effects on air quality and climate. The climatic effects are caused both by direct sunlight scattering effects and by indirect effects due to the influence of secondary aerosols on the cloud formation and their properties. It has been estimated that 46–82% of SO_2 will form sulphate particles in the atmosphere (IPCC, 2001). In one of our previous studies, Sippula et al. (2009c) compared the particle emissions from small heavy fuel oil (HFO) and wood-fired boilers. One conclusion of that study was that the quantity of the particle emissions as well as their physical and chemical properties are clearly different between heavy fuel oil and wood combustion. Thus, the use of wood and fossil fuel oils would be predicted to have a very different impact on both human health and the environment. With efficient wood combustion systems, the particle emissions are mainly composed of ash species such as alkali metal chlorides and sulphates, but unfortunately when the combustion conditions are not optimal, more organic compounds such as polycyclic aromatic hydrocarbons (PAHs) are formed (Tissari et al., 2008; Sippula et al., 2009a; Hays et al., 2011; Aurell et al., 2012; Kinsey et al., 2012). The particles from the oil combustion usually contain soot, organic material and significant amounts of sulphur, depending on the oil sulphur content and combustion quality (Hays et al., 2008; Sippula et al., 2009c). The HFO particles typically contain also substantial amounts of heavy metals (Hays et al., 2009; Sippula et al., 2009c).

Previous epidemiological studies have shown that ambient particles which originated from fossil fuel combustion are especially harmful to health (Laden et al., 2000; Lanki et al., 2006; Penttinen et al., 2006). Toxicological studies have also shown that particles from fossil fuel combustion may cause adverse effects (e.g. Jalava et al., 2006; Happo et al., 2008). The toxicity of the emissions from oil combustion is often associated with the high metal concentrations, especially Ni and V from heavy fuel oil having been associated with toxic effects (e.g. Molinelli et al., 2006). However, also emissions from wood combustion have exerted toxic properties in several studies (Kocbach Bølling et al., 2009; Danielsen et al., 2011; Tapanainen et al., 2011; Jalava et al., 2012; Tapanainen et al., 2012). In epidemiological studies, it has been confirmed that small-scale wood combustion is associated with adverse health effects (Andersen et al., 2007; Naeher et al., 2007; Sarnat et al., 2008). Wood combustion emissions may also have an influence on the emergence of asthma and other respiratory symptoms (Boman et al., 2003; Allen et al., 2008; Ghio, 2008).

Even though there are many studies examining energy production related emission sources, there are no comparisons available helping to decide which energy sources should be favoured in order to reduce the adverse health effects in humans. If one wishes to estimate the optimal way to produce energy, one needs to perform a comprehensive examination of the emissions. In other words, the toxicity of emissions from wood and fossil fuel combustion need to be compared, not simply the overall emission levels.

This work is a continuation study to evaluate the toxicological effects of the emissions from fossil fuel oil and wood combustion and to compare the new results with those obtained in the previous study. The aim of this study was to compare four alternative ways of producing decentralized energy for use in small communities with respect to their flue gas emissions and the toxicological properties of emissions. Two different size classes of boilers were examined, the small scale (20–25 kWth) and the medium scale (4–15 MWth), and the use of fossil oil fuels was compared against wood fuels. A modern small-scale pellet boiler and a small-scale district heating plant with a rotating grate combustion unit represented the energy production of the wood combustion, and a small-scale light fuel oil (LFO) burner and heating boiler with a HFO burner represented fossil fuel combustion. Gaseous and particulate emissions were measured from the flue gas and the cytotoxicity of the particulate emissions was examined.

2. Material and methods

2.1. Combustion appliances and fuels

Details of the measurement and dilution systems and the combustion appliances are presented in Table 1. In this study, a pellet boiler and a light fuel oil burner represented small-scale combustion systems as their nominal output was in the range of 20–25 kW. Pellet appliance was a fully automated grate boiler, described in detail by Lamberg et al. (2011a, 2011b). The light fuel oil burner was a conventional oil burner with pressurized atomization commonly used in residential heating systems. The light fuel oil burner was maintained before the measurements. Rotating grate combustion unit (nominal output of 10–15 MW) and heavy fuel oil burners (nominal output of 4–7 MW) represented medium-scale combustion systems. The rotating grate combustion unit included a cyclone and a single field ESP with horizontal flow fields to remove coarse and fine particles from the flue gas. The technology of the rotating grate has been detailed and visualized by Sippula et al. (2009a). In the present study, all the wood combustion measurements were conducted after the cyclone. Heavy fuel oil burners with pressurized atomization did not include any flue gas filtration systems. The small-scale appliances were operated in the emission research laboratory at the University of Eastern Finland and the medium-scale appliances in field. The properties of wood chips, wood pellets, LFO and HFO fuels are presented as a Supplementary material. The LFO burner, pellet boiler and wood boiler were operated continuously but the HFO burner was operated intermittently due to the low energy demand during the measurement campaign. The sampling was turned off when the burner was on the break and it was not continued until the burner was turned on again and the residual oxygen concentration in the flue gas was restored to its normal level.

Emission results for various appliances from our previous studies (Lamberg et al., 2011a,b; Sippula et al., 2009a; and Sippula et al., 2009c) were compared to three appliances examined in this study. The combustion appliances, the fuels and the dilution and

Table 1
Combustion appliances, outputs, fuels, filtration techniques, measurement instruments and dilution systems. Subjects of the present study are marked with grey background.

	Wood before and after ESP 1	LFO	HFO 1	Pellet	Wood before and after ESP 2	Wood before and after ESP 3	HFO 2	HFO 3	HFO 4
Reference				Lamberg et al. (2011a)	Sippula et al. (2009a)	Sippula et al. (2009a)	Sippula et al. (2009c)	Sippula et al. (2009c)	Sippula et al. (2009c)
Combustion appliance	Rotating grate combustion unit	Light fuel oil burner	Heavy fuel oil burner	Modern pellet boiler	Rotating grate combustion unit	Rotating grate combustion unit	Heavy fuel oil burner	Heavy fuel oil burner	Heavy fuel oil burner
Nominal output	10 MW	20 kW	5.2 MW	25 kW	15 MW	10 MW	4 MW	7 MW	4 MW
Fuel	Wood chips	Light fuel oil	Heavy fuel oil	Pellet	Wood chips	Sawdust and bark	Heavy fuel oil	Heavy fuel oil	Heavy fuel oil
Flue gas filtration	Cyclone, ESP	–	–	–	Cyclone, ESP	Cyclone, ESP	–	–	–
Measurement instruments	FTIR, DGI	ELPI, FTIR, PM_1 filters (OC/EC), DGI, aspiration sampler (TEM)	FTIR, DGI	ELPI, FTIR, PM_1 filters (OC/EC), DGI, aspiration sampler (TEM)[a]	ELPI, FTIR, PM_1 filters (OC/EC)	ELPI, FTIR, PM_1 filters (OC/EC)	ELPI, FTIR, PM_1 filters (OC/EC)	ELPI, FTIR, PM_1 filters (OC/EC)	ELPI, FTIR, PM_1 filters (OC/EC)
Dilution for PM_1 filters	–	PRD + ED	–	PRD + ED	PRD	PRD	PRD	PRD	PRD
Dilution for ELPI	–	PRD + ED + ED	–	Dilution tunnel	PRD	PRD	PRD	PRD	PRD
Dilution for DGI	PRD	PRD	PRD	PRD	–	–	–	–	–
Flue gas temperature	133–139 °C[b]	81 ± 3 °C	143 ± 0.1 °C						
Sampling temperature (DGI)	34 ± 3 °C	35 ± 4 °C	32 ± 6 °C						

[a] TEM samples were taken in another experiment but from the same appliance.
[b] Based on uncontinuous measurement, average and standard deviation is not possible to define.

the sampling methods used in the earlier studies were well comparable to those of this study.

2.2. Experimental set-up

Fig. 1 shows the experimental set-up. Gaseous compounds were measured continuously from the stack by a Fourier transform infrared analyser (FTIR, Gasmet Technologies Ltd.) in all experiments except for the one with pellet combustion. The O_2 concentration was measured with a separate CrO cell which was integrated with an FTIR analyser. In pellet combustion NO, NO_2, CO, CO_2 and O_2 were measured by a gas analyser system (ABB, Cemas Gas Analysing Rack). Flue gas temperatures were measured continuously from undiluted and diluted flue gas using K-type thermocouples.

Flue gas for a Dekati gravimetric impactor (DGI, 70 lpm, Dekati Ltd.) was diluted with a porous tube diluter (PRD). The samples were collected with DGI with cut-off sizes 0.2, 0.5, 1.0 and 2.5 μm and with a back-up filter. Toxicological responses and PAH, ion and element contents of the particulate emission samples were assessed and compared. A detailed description of DGI sampling and filter handling procedure has been recently provided by Ruusunen et al. (2011). In wood combustion, the samples before and after the ESP were taken one after the other, not in parallel.

PM_1 samples for the organic (OC) and elemental carbon (EC) analyses were collected on 47 mm quartz fibre filters (Pallflex, Tissuquartz) with stainless steel filter holders (Gelman Sciences Inc., model 2220). A pre-impactor (Dekati Ltd.) removed the particles if their aerodynamic diameter was larger than 1 μm. Filters were weighed before and after the collection in a weighing room with the temperature (20 °C) and the relative humidity (40%) controlling. Filters were kept in the weighing room for at least 24 h prior to weighing in order to allow them to stabilize. Gravimetric analyses were performed with a microbalance of 1 μg sensitivity

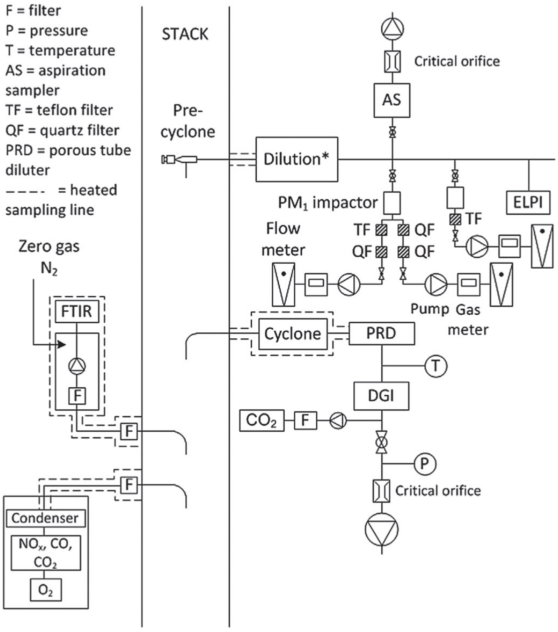

Fig. 1. Experimental set-up. *PRD + ejector diluter in LFO, HFO and wood combustion measurements; dilution tunnel in pellet combustion measurements.

(Mettler Toledo, MT5) with a Staticmaster Po-210 charge eliminator.

An electrical low pressure impactor (ELPI, 10 lpm, sintered impactor plates, Dekati Ltd.) with a cut-off size from 24 nm to 9.38 μm was used to measure particle number emissions and number size distributions from the diluted flue gas.

Samples for electron microscopes were collected on holey carbon copper grids using an aspiration sampler (Lyyränen et al., 2009). The samples were analysed using field emission transmission electron microscopes (TEM, Philips CM-200 FEG/STEM and JEOL JEM 2100F FEG/STEM, both operated at 200 kV) equipped with an energy dispersive X-ray spectrometer (EDS).

The dilution for PM_1 samples, TEM samples and ELPI was carried out with PRD and ejector diluter (ED) with the exception of the pellet combustion measurements where the flue gas for ELPI was diluted in a dilution tunnel (ISO 8178-1, 1996; Lamberg et al., 2011a, 2011b). The dilution with the PRD and ED has been described elsewhere (Lyyränen et al., 2004; Tissari et al., 2007). All the dilution ratios were calculated from the CO_2 concentrations of the undiluted and diluted flue gas as described by Sippula et al. (2009a). The results were corrected with dilution ratios and calculated in relation to fuel energy input to the combustion process (SFS 5624, 1990).

2.3. Chemical analyses

A wide array of elements (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sr, Th, Ti, Tl, U, V, and Zn) and ions (Cl^-, Br^-, F^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) were determined from the PM_1 samples collected with DGI. Samples for elemental analysis were eluted with $HF–HNO_3$ acid and analysed with an inductively coupled plasma mass spectrometer (ICP-MS, Perkin Elmer Elan 6000, Pakkanen et al., 2001) and the samples for ion analysis with deionized water prior to analysis with an ion chromatograph (IC, Dionex ICS-2000) system (Teinilä et al., 2000).

OC, EC and carbonate carbon (CO_3) were analysed from the PM_1 samples collected on the quartz filters. The analyses were performed by a thermal-optical method using an OCEC carbon aerosol analyser (model 4 L, Sun Laboratories Inc.). This analysis is based on the protocol in use in National Institute for Occupational Health (NIOSH 5040, 1999).

PAHs (30 compounds) were analyzed with a gas chromatograph mass spectrometer (6890N GC, equipped with a 5973 inert Mass Selective Detector, Agilent Technologies). A DB17-MS column was used for the separation of the compounds. The analysis was operated with selected ion monitoring (SIM) mode. The quantification limit of the method was 0.1 ng mg^{-1}. A detailed description of the PAH analysis has been recently presented by Lamberg et al. (2011a).

2.4. Toxicological analyses

There are numerous biological mechanisms that are responsible for the adverse health effects, e.g. cytotoxicity, inflammation, genotoxicity and oxidative stress associated responses (Binkova et al., 2003; Tao et al., 2003; Pope and Dockery, 2006). In our previous studies, cytotoxicity has been found to provide a good estimate of toxicological responses of wood combustion emissions in general and therefore in this study, cytotoxicity was chosen to represent toxicological responses (Jalava et al., 2006,2012). A wider range of toxicological responses will be presented in a separate article. A mouse macrophage cell line RAW264.7 was cultured in complete RPMI 1640 cell culture medium at +37 °C and in a 5% CO_2 atmosphere. In the experiments, the cell suspension was diluted to 5×10^5 cells ml^{-1} and cultured on 6-well plates (Costar, Corning, NY, USA) for 24 h prior to experiments.

Before the cell exposure, particulate sample tubes were treated in an ultrasonic water bath for 30 min to suspend the PM_1 samples into pyrogen free water (Sigma W1503, St. Louis, MO, USA) at a concentration of 5 mg ml^{-1}. Cells were exposed to four doses (15, 50, 150 and 300 μg ml^{-1}) of each particulate sample for 24 h in three independent experiments that were made in duplicate. Untreated cells as well as blank samples were used in the experiments as controls for the exposed cells.

After the 24-h exposure, the cells were suspended into cell culture medium by scraping them from the bottoms of the wells. In all, 2 × 100 μl of cell suspension from each well were taken for the MTT analysis of cytotoxicity. The remaining cell suspension was stored for further toxicological analyses, including inflammation and other cytotoxic mediators.

In the MTT-test, the viability of the macrophages was measured on 96-well plates. The absorbance was detected with a plate reader and the viability was calculated as a percentage from the corresponding readings from control cells (Jalava et al., 2005). The MTT-test is based on the metabolic activity of the macrophage cells i.e. the presence of functioning mitochondria in the cells. The method was tested for absorbance from particulate samples only to rule out any methodological errors.

3. Results and discussion

3.1. Gaseous and particulate emissions

Gaseous and particulate emissions are presented in Table 2. It was postulated that the ESP would have no effect on the gaseous emissions and thus they were measured only before ESP. Wood chip, LFO and HFO combustion produced only small amounts of CO. In Wood combustion before ESP 1, LFO and HFO 1, the measured CO emissions were below the detection limit of the FTIR. Although the CO emission in pellet combustion was the highest measured in this study, 80 mg MJ^{-1}, this is still only a moderate emission level for example when compared to batch combustion where the CO emission is in the range 390–2700 mg MJ^{-1} (Lamberg et al., 2011a). NO_x emissions were found to vary greatly between different devices. The highest NO_x emissions were observed with HFO combustion. HFO combustion produced also very high SO_2 emissions whereas in other experiments, especially in wood chip and pellet combustion, the SO_2 emissions were found to be low, as expected since the sulphur contents of wood fuels were low (see Supplementary material).

The lowest PM_1 emission was encountered with LFO combustion, 0.1 mg MJ^{-1}, but also with Wood combustion after ESP 1 the emission was low, 0.6 mg MJ^{-1} (Table 2). Probably due to the different fuel and appliance used, the emission in the LFO combustion was much lower than that measured previously by Hays et al. (2008). With Wood after ESP (cases 2–3) and in HFO combustion (cases 2–4), the PM_1 emissions were moderate ranging from 4 mg MJ^{-1}–8.3 mg MJ^{-1}. With HFO 1 and Pellet, the PM_1 emissions were somewhat higher, 20.3 mg MJ^{-1} and 16.2 mg MJ^{-1}, respectively. With pellet combustion, the emission was close to the values measured in previous studies (Tissari et al., 2008; Schmidl et al., 2011). With Wood before ESP, especially in case 1, the PM_1 emissions were as high as 264 mg MJ^{-1}.

3.2. PM_1 chemical composition

Based on the results from ICP-MS and IC analyses (Fig. 2), with pellet and wood chip combustion, the main element found in the analysis of PM_1 was potassium which accounted for 37% and 41–49% of PM_1, respectively. In addition, Na^+, Cl^- and SO_4^{2-} were

Table 2
Particle and gas emissions.

		Wood before ESP 1	Wood after ESP 1	LFO	HFO 1	Pellet	Wood before ESP 2–3	Wood after ESP 2–3	HFO 2-4
Reference						Lamberg et al., 2011a	Sippula et al., 2009a	Sippula et al. 2009a	Sippula et al., 2009c
H_2O	%	23.3 ± 1.1	n.m.	10.5 ± 0.6	10.4 ± 0.2	≈7	≈24	≈24	7.5–7.9
O_2	%	7.7 ± 0.5	n.m.	5 ± 0.2	4.3 ± 0.5	11.9 ± 0.93	4.6–5	4.6–5	2.8–6.2
CO	mg MJ^{-1}	<AR[a]	n.m.	<AR[a]	<AR[a]	80 ± 67	6.6 ± 0.6–12	n.m.	1.4–2.5 ($n = 2$)
NO_x (as NO_2)	mg MJ^{-1}	146 ± 9	n.m.	85 ± 2	317 ± 15	73 ± 3	33–156 ± 4	n.m.	166–183 ($n = 2$)
SO_2	mg MJ^{-1}	<AR[b]	n.m.	22 ± 2.3	595 ± 22	<AR[b]	0.017 ± 0.029 ($n = 1$)	n.m.	338–423 ($n = 2$)
N_{tot}	MJ^{-1}	n.m.	n.m.	4.9E + 05 ± 8.0E + 04	n.m.	3.5E + 13 ± 8.0E + 12	2.7E + 13 ± 1.2E + 13 ($n = 1$)	6.1E + 11 ± 3.4E + 11–6.5E + 12 ± 1.4E + 12	1.7E + 13 ± 2.1E + 12–2.1E + 13 ± 4.0E + 11
PM_1 (DGI)	mg MJ^{-1}	264 ± 40	0.6 ± 0.1	0.1 ± 0.02	20.3 ± 8.6	16.2[c]	77–92 (BLPI)	4–6 (BLPI)	4.1–8.3 (BLPI)
GMD	nm	n.m.	n.m.	30 ± 3	n.m.	60	100 ± 9	147 ± 7–216 ± 7	49 ± 1–61 ± 1 ($n = 2$)
OC	mg MJ^{-1}	n.m.	n.m.	0	n.m.	0.9 ± 2.1	0.55 ($n = 1$)	0.14 ($n = 1$)	0.03–0.38 ($n = 2$)
EC	mg MJ^{-1}	n.m.	n.m.	0.0116	n.m.	0.1 ± 0.17	0.19 ($n = 1$)	0.081 ($n = 1$)	0.20–0.66 ($n = 2$)
CO_3	mg MJ^{-1}	n.m.	n.m.	n.m.	n.m.	1.2 ± 1.1	0.38 ($n = 1$)	0.1 ($n = 1$)	n.m.

BLPI = Berner Low Pressure Impactor.

[a] Below accuracy range 100 ppm.

[b] Below accuracy range 20 ppm.

[c] Tapanainen et al., 2011.

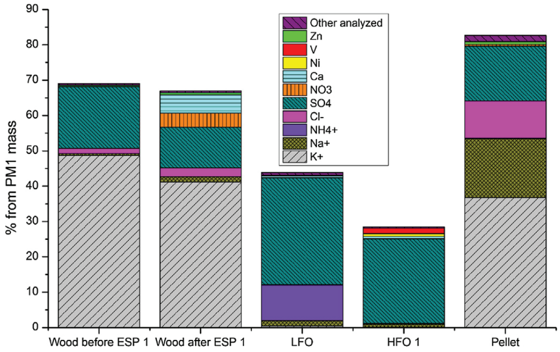

Fig. 2. The main ash species in the PM1. IC results from pellet combustion are presented also by Lamberg et al. (2011a) and Tapanainen et al. (2011).

found to be present in the wood chip combustion derived particles. These four compounds accounted for 57–79% of the total PM_1. In addition, values of 0.4–0.8% of Zn were detected from pellet and wood chip combustion particles. K, Cl, SO_4, Na and Zn are all common compounds in biomass combustion particles (e.g. Sippula et al., 2009a).

There were differences in the chemical composition of wood chip combustion particles before and after the ESP. In the particles collected after the ESP, significant amounts of NO_3^- and Ca were found. In our opinion, the differences can be due to the change in the fuel composition during the measurements as well as due to the size-dependent collection efficiency of the ESP. The separation efficiency of the ESP varies as the function of the particle size and therefore some elements might become enriched in the flue gas after the ESP. This is particularly true for Ca, which is known to be present mainly above the particle size 0.2 μm (Sippula et al., 2009a) whereas the lowest filtration efficiency of an ESP is usually found between 0.2 and 2 μm (Lind et al., 2003; Sippula et al., 2009a). In addition, the wood chip fuel was sawmilling residue in which the bark content can vary extensively. Both the particle and the gaseous emissions as well as the humidity of the flue gas were found to vary during the measurement campaign, evidence that the fuel composition varied. However, because only one fuel sample was taken, the fuel variation cannot be verified with certainty.

Sulphate was one of the main fine particle components contributing 30% and 24% of the PM_1 mass in the LFO and HFO combustion, respectively. Both PM_1 samples contained also a small amount of Na^+ and Ca. In addition, particles from LFO combustion contained 10% of NH_4^+. Particles from the HFO combustion included 1.5% of V and 0.9% of Ni. The amount of these metals were higher than observed in the study of Hays et al. (2009) where the amount of all analyzed trace metals was <0.1% of $PM_{2.5}$. This is possible due to the differences in the used fuel and the combustion appliance.

The carbon in PM_1 of LFO and HFO combustion particles was mainly composed of EC (Table 2). HFO combustion derived particles contained also a small amount of OC. In contrast, in pellet and wood chip combustion particles, the carbon fraction was mainly composed of OC and CO_3. However, it must be noted that the determined OC fractions are relatively small, when compared to batch-wise fired combustion appliances, for example.

In particular, in HFO and in LFO combustion, the chemical mass balance of the samples was rather poor: only 44% and 28% of the PM_1 could be identified, respectively. However, since most of the identified parts of the samples was sulphur, mainly in the form of sulphuric acid (see chapter 3.4), there is most likely also a significant fraction of water bound into the particles which explains the large fraction of the unidentified mass (Ristimäki et al., 2010).

3.3. PAH emissions

The highest PAH content in PM_1 was found in the LFO combustion derived particles where PAHs accounted for 1.7% of PM_1 mass (Table 3). In addition, the highest genotoxic PAH concentration (genotoxic PAHs listed in Table 3) in PM_1 sample was taken from LFO combustion. However, the highest PAH emission (0.2 mg MJ^{-1}) was encountered in HFO combustion. The smallest PAH emission as well as the proportion of PAHs in PM_1 was observed in pellet combustion. The most common PAH compounds found from the samples Wood before ESP 1, Pellet and LFO were fluoranthene and pyrene. Those compounds were among the most common PAH compounds in wood combustion also in the previous studies (Tissari et al., 2007; Kaivosoja et al., 2012). Besides fluoranthene and pyrene, also benzo[c]phenanthrene, benzo[a]anthracene and chrysene were common in the samples collected from wood combustion after ESP. The most common PAH compounds detected in HFO combustion were benzo[b]fluoranthene, chrysene, benzo[k]fluoranthene and benzo[j]fluoranthene. Overall, oil combustion produced higher amount of PAHs than the wood combustion. In addition, greater amounts of heavier PAHs, which are known to be more harmful to health than the lighter PAHs, were detected from the oil combustion derived PM_1 than from the wood combustion derived PM_1.

Table 3
PAH content in PM_1 (ng mg^{-1}), sum of 30 PAHs PM_1 (ng mg^{-1}; mg MJ^{-1}) and sum of genotoxic PAHs PM_1 (ng mg^{-1}). The genotoxic PAHs (WHO-ICPS, 1998) are typed in bold. PAH results from pellet combustion are presented by Lamberg et al. (2011a) and Tapanainen et al. (2011).

PAHs in PM_1 (ng mg^{-1})	Wood before ESP 1	Wood after ESP 1	LFO	HFO 1	Pellet
Naphthalene	<DL	<DL	4.8	<DL	0.2
Acenaphthylene	<DL	<DL	2.3	<DL	<DL
Acenaphthene	<DL	<DL	4.1	<DL	<DL
Fluorene	<DL	<DL	31	<DL	<DL
Phenanthrene	0.8	2.1	335	80	0.6
Anthracene	<DL	<DL	19	2.8	<DL
1-Methylphenanthrene	<DL	<DL	206	13	0.1
Fluoranthene	20	172	4314	533	1.7
Pyrene	24	310	4685	53	2.1
Benzo[c]phenanthrene	0.8	100	839	400	0.1
Benzo[a]anthracene	0.8	278	2060	773	0.1
Cyclopenta[c,d]pyrene	<DL	<DL	120	<DL	0.2
Triphenylene	0.2	36	354	242	0.1
Chrysene	0.8	222	2071	1778	0.1
5-Methylchrysene	<DL	<DL	<DL	1.5	<DL
Benzo[b]fluoranthene	<DL	25	486	2153	0.1
Benzo[k]fluoranthene	<DL	14	285	1637	<DL
Benzo[j]fluoranthene	<DL	19	342	1002	0.1
Benzo[e]pyrene	<DL	14	276	687	0.2
Benzo[a]pyrene	<DL	8.1	250	25	0.1
Perylene	<DL	<DL	28	14	<DL
Indeno[1,2,3-cd]pyrene	<DL	<DL	68	250	<DL
Dibenzo[a,h]anthracene	<DL	<DL	6.6	66	<DL
Benzo[g,h,i]perylene	<DL	<DL	208	170	0.2
Anthanthrene	<DL	<DL	11	<DL	<DL
Dibenzo[a,l]pyrene	<DL	<DL	<DL	<DL	<DL
Dibenzo[a,e]pyrene	<DL	<DL	<DL	<DL	<DL
Coronene	<DL	<DL	53	26	<DL
Dibenzo[a,i]pyrene	<DL	<DL	<DL	<DL	<DL
Dibenzo[a,h]pyrene	<DL	<DL	<DL	<DL	<DL
Sum of 30 PAHs (ng mg^{-1})	*47*	*1200*	*17,060*	*9906*	*6.0*
Sum of genot. PAHs (ng mg^{-1})	*23*	*887.64*	*11,978*	*9770*	*3.0*
Sum of 30 PAHs (mg MJ^{-1})	*0.013*	*0.0007*	*0.0015*	*0.20*	*0.0001*
$PAHs/PM_1$ (%)	*0.005*	*0.12*	*1.7*	*0.99*	*0.0006*

<DL = below detection limit.

3.4. Particle number emissions, size and structure

With wood combustion, the ELPI measurements were conducted downstream of the ESP. With LFO combustion, the number emission was lowest and also the geometric mean diameter (GMD) was smallest (Fig. 3). The number size distribution in LFO combustion was found to be bimodal. The larger mode was found to compose of soot agglomerates, of which typical examples are illustrated in Fig. 4a and b, observed with the TEM. Fig. 4c shows details of a soot agglomerate at high resolution TEM micrograph (the complete agglomerate is shown in the insert and the area of the HR-TEM image is indicated by a square). The mode in the smaller particles was assumed to be composed of sulphuric acid particles since it is known that sulphuric acid tends to nucleate during dilution with ambient air, forming a large number of nanoparticles (Shi and Harrison, 1999). This was confirmed by TEM and corresponding EDS analyses; in Fig. 4b the holey carbon film is decorated with small sulphate acid particles (one indicated with a white circle). The analyses indicate that in LFO combustion the mode in the smaller particles was composed of sulphuric acid particles and the mode in the larger particles of soot particles.

With wood combustion, the GMDs of the particles were larger than in other cases, an average of 100 nm before the ESP and 147–216 nm after the ESP. The peak in the particle number size distribution occurred approximately in the same size range where the separation efficiency of the ESP is at its poorest (see chapter 3.2).

The TEM micrographs and the corresponding EDS analyses indicate that the typical pellet combustion particles, present at various sizes and shapes (Fig. 5a and b), consisted mostly of K, S, Cl, and Na. These elements are known to be in form of alkali metal sulfates and chlorides (Sippula et al., 2007). In addition, large amounts of C were found locally, marked with a ring in Fig. 5c. Evidence of Zn was found from some (Fig. 5b, the large dark nucleus), but not all, observed particles. It is known that Zn from the fuel is usually released in the fine particle fraction (Sippula et al., 2009b). In the current case, as the conditions for pellet combustion were oxidizing, the zinc was expected to appear in oxidized form (Jöller et al., 2005).

3.5. Toxicity

The particulate mass emitted from wood chip combustion was clearly the least potent in its ability to induce cytotoxicity in macrophages (Fig. 6). It exerted lower responses than the particulate sample from pellet combustion. The responses to pellet combustion

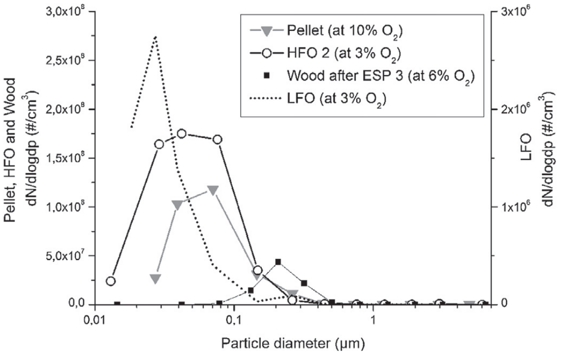

Fig. 3. Particle size distributions measured by ELPI. Pellet combustion results are adapted from Lamberg et al. (2011a), wood combustion results from Sippula et al. (2009a) and HFO combustion results from Sippula et al. (2009c).

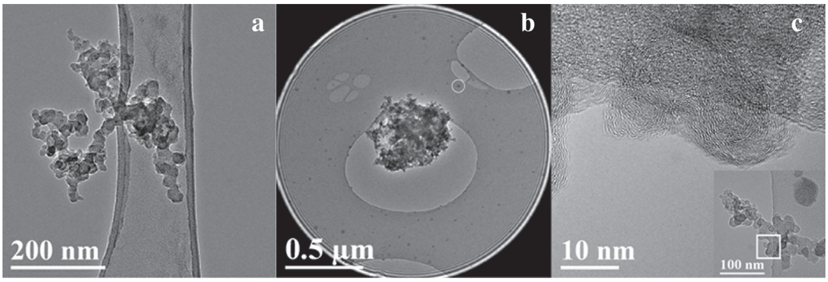

Fig. 4. TEM micrographs of fine particles collected from LFO combustion.

sample were slightly higher than those seen in our previous study with different small-scale heating systems (Jalava et al., 2012). However, the pellet material or the pellet boiler in that study was not the same as in the present study. These differences in responses most probably originate from differences in particle chemical composition. It is also noteworthy that the dose response curves for each case are different, which makes also direct comparison between the samples more complex; the order of their toxic potency is different, depending on the dosage level. We have also previously observed greatly variable chemical compositions and toxicological activities between the different combustion situations (Jalava et al., 2012). Both the PAH compounds in poorly controlled combustion processes and metal oxides in good combustion may be responsible for the toxic activity (Jalava et al., 2012; Happo et al., 2013).

Compared to the wood fuels, both LFO and HFO combustion led to emissions of more cytotoxic particulate mass. At higher doses, there was a greater difference in the responses from wood combustion particles. A comparison between particles from two oil fuels revealed that at the two highest doses, the emissions from HFO were more cytotoxic than those from LFO. However, with lower doses, the order between those samples was in the opposite direction. Unlike the samples from combustion of wooden fuels, both the oil fuels had a certain threshold concentration between 50 and 150 $\mu g\ ml^{-1}$. There is very limited information available on toxicity of emissions from LFO fired boilers. However, there is one study where emissions have been evaluated from the LFO burners (Hays et al., 2008). The soot from burners may contain potentially harmful components. Furthermore, there are many studies of distillate oil fuel use in engines. Diesel engine emissions have been indicated as being cytotoxic in many previous studies (e.g. Jalava et al., 2010; Hemmingsen et al., 2011).

HFO combustion has been claimed to be harmful in many epidemiological studies (e.g. Laden et al., 2000; Janssen et al., 2002). HFO combustion produces particulate emissions that are mostly composed of sulfates. The role of sulphate aerosol is not considered to be one of the most important causes for adverse health effects, but the acidic sulfates may have relevance for asthmatics (Schlesinger and Cassee, 2003). The samples in the present study have not gone through atmospheric transformation processes and therefore it is possible that the toxicology profile is different compared to the same emission sources in the atmosphere. There have been clear indications that oil combustion, Ni and V as tracers, have induced significant toxicological responses in both cells and animals (Dye et al., 2001; Happo et al., 2008). In the present study, the clearest difference between the two oil combustion samples was detected in their metal concentrations. This almost certainly explains the difference observed between the cytotoxicity of the samples.

One interesting feature of this data was that particles collected after ESP in wood combustion were significantly more cytotoxic than those collected before the ESP in the same district heating plant. One possible explanation may be the different chemical compositions in these two samples. As the largest observed difference, the sample collected after ESP clearly contains a larger proportion of calcium which has been identified as a causative toxic agent also in previous studies (Happo et al., 2008; Jalava et al., 2009). Another explanation for the increased toxicity would be higher Zn content of the particles after ESP and third, the enrichment of PAH compounds to the sample after ESP. Compared to the oil combustion derived samples PAH concentrations were still much lower. The ESP also changes the physical properties of the particles, including size, shape and surface area. This may be one reason of the differences since these parameters are known to affect toxicological responses of nanoparticles (Oberdörster et al., 2006). However, at the same time when toxicity per same mass increased, the emissions after the ESP were decreased to a small fraction from the untreated emission. Therefore, the emissions after ESP should probably not be considered as more harmful. This

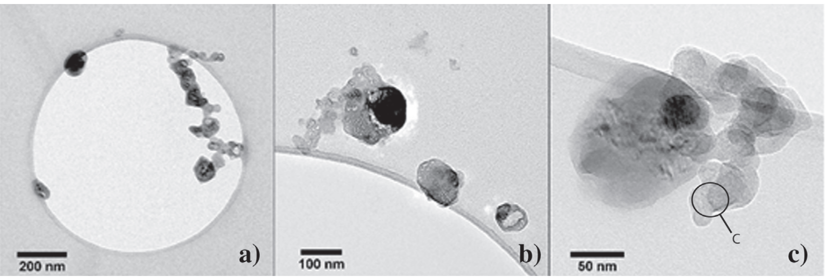

Fig. 5. TEM micrographs of fine particles collected from pellet combustion. Particles either lie on thin carbon surface (grey background), or are attached on the edges of holes (lighter background) in the substrate.

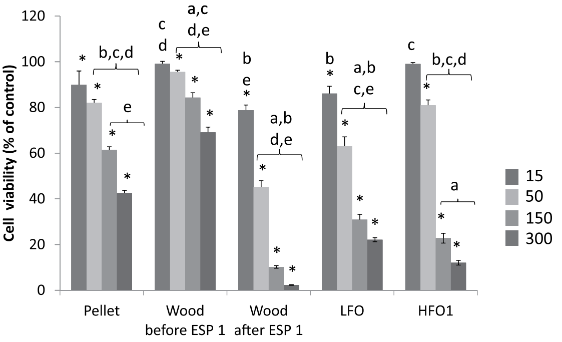

Fig. 6. Cell viability after 24 h' exposure of mouse RAW264.7 macrophages to four doses (15, 50, 150 and 300 μg ml^{-1}) of particulate samples from different heating systems. Asterisks indicate statistical significance to control (Dunnet's test $p < 0.05$). Letters indicate statistical difference to other samples (a = Pellet, b = Wood before ESP 1, c = Wood after ESP 1, d = LFO and e = HFO 1) at each dose. Results for comparison with pellet boiler adapted from Tapanainen et al. (2011).

phenomenon will still require more research to know the exact health effects of the after treatment technologies.

In the present article, cytotoxicity, one important mechanism was chosen to present toxicity of the different emissions. There are however, many other mechanisms that can be affected by these emissions and they need further investigation. Combining the emission characterization and full coverage of toxicological responses will give a tool for evaluating the relative harmfulness of energy production alternatives and use this information in the regulatory decision processes.

4. Conclusions

In this study, four energy production alternatives were compared with respect to their flue gas emissions and the cytotoxicity of the emissions. From the toxicological point of view, the HFO combustion was found to be the worst energy production option. It also produced the largest SO_2 and PAH emissions and its PM_1 emission contained harmful metals such as vanadium and nickel. These metals possess a large cytotoxic potential in the cells. The overall toxicological effects of oil combustion samples were greater than the corresponding samples from wood combustion.

Wood combustion represents a competitive option to combustion of fossil fuels. The PM_1 from wood combustion was composed mainly of alkali metals such as potassium and a low PM_1 emission could be achieved by installing an efficient filtration system such an ESP. However, the small amount of particles passing through the ESP still evoke toxic effects. Overall, lower emissions should be preferred, in order to decrease the particulate levels in the atmosphere, but also these low emission technologies may have toxic potential.

Nowadays, the amounts of particle and gaseous emissions from energy production and industrial plants are mainly controlled by the environmental licence or the legislation. However, the toxicity of the emissions may vary drastically between various energy production alternatives, as was also shown in this study. We propose that in the long term, in addition to the emission amounts, also the toxicity of the emissions should be taken into account when regulating the emission limits for the plants.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.05.014.

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Table. Fuel properties. HFO 1, LFO and Wood 1 are the fuels used in the present study. Wood 2, Pellet and HFO 2 are the fuels used in the previous studies. The results are presented as mg kg^{-1} of fuel and as mass percentages of fuel. Heating values are presented as MJ kg^{-1}.

		Wood 1[a]	HFO 1	LFO	Wood 2 [a]	Pellet [a]	HFO 2
Reference					Sippula et al., 2009a	Lamberg et al., 2011a	Sippula et al., 2009c
Ag	mg kg^{-1}						
Al	mg kg^{-1}	120			89–170 (n=2)	0.76	
Ba	mg kg^{-1}				17.9–32 (n=2)		
Ca	mg kg^{-1}	6100			1740–2900 (n=2)	892	
Cd	mg kg^{-1}				0.09–0.23 (n=2)		b.d.
Cl	mg kg^{-1}	100	<200	<5	75–1520 (n=2)	10	60–400 (n=3)
Co	mg kg^{-1}				0.2 (n=1)		
Cr	mg kg^{-1}	0.67	<10	<10	1.1–2.2 (n=2)		0.9–14 (n=2)
Cu	mg kg^{-1}	2.7	<10	<10	1.3–4.1 (n=2)	1.37	b.d.
Fe	mg kg^{-1}	72			67–454 (n=2)	44.3	
H	m-%		10.5	12.9			
K	mg kg^{-1}	1600			1070–1470 (n=2)	420	
Li	mg kg^{-1}						
Mg	mg kg^{-1}	550			357–400 (n=2)	142	
Mn	mg kg^{-1}	340	<10	<10	141–170 (n=2)	82	0.54–2.1 (n=2)
N	m-%	0.24	0.34	0.03			
Na	mg kg^{-1}	41			24–25.7 (n=2)	180	
Ni	mg kg^{-1}	0.67	25	<10	0.62–0.78 (n=2)	0.33	22–25 (n=3)
P	mg kg^{-1}	420			169–245 (n=2)	58	
Pb	mg kg^{-1}		<10	<10	0.41–0.62 (n=2)		2.9 (n=1)
Rb	mg kg^{-1}				4.3–5.7 (n=2)		
S	m-%	<0.02	0.982	0.023	128–190 (n=2)	<0.02	0.75–0.91 (n=3)
Si	mg kg^{-1}	150			78–185 (n=2)		
Sr	mg kg^{-1}				9.4–13.6 (n=2)		
V	mg kg^{-1}		25	<10	0.13 (n=1)		29–52 (n=3)
Zn	mg kg^{-1}	92	<10	<10	23–42 (n=2)	<1	b.d.
Moisture	m-%	55.33			47–50.9 (n=2)	8.1	
Ash	m-%	1.7	0.029	<0.001		0.3	0.03–0.05 (n=3)
Gross calorific value	MJ kg^{-1}	20.37	42.417	45.618			
Net heating value	MJ kg^{-1}	19.06	40.18	42.883	19.2–19.3 (n=2)	19	

[a] The elemental analysis results are presented as mg kg^{-1} of dry fuel